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BACTERIOLOGICAL ANALYSIS OF SOME LONG CORES OF MARINE SEDIMENTS

By

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Until recently only the uppermost layers of marine sediments have been generally available for scientific investigations since most coring instruments obtained samples less than a meter long. The early bacteriological investigations of Certes (1884), Russell (1892), Fischer (1894), Gazert (1912), and Drew (1912) were confined to surface samples obtained by dredging. Lloyd (1931) was the first to report quantitative data on the vertical distribution of bacteria in subsurface layers of marine sediments. Similar investigations were made by Reuszer (1933), and Waksman et al. (1933). ZoBell and Anderson (1936) and ZoBell (1938) enumerated both aerobic and anaerobic bacterial populations. The longest core on which quantitative results have been published was 68 centimeters long (ZoBell and Anderson, 1936) although Waksman et al. (1933) have reported the occurrence of anaerobes down to a depth of 90 centimeters.

There are certain problems whose solutions require information on the depth to which bacteria may be present and active in marine sediments. For this reason the bacteriological analysis of as deep strata

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as possible is desirable. As an example of such problems it is sufficient to mention the controversy over the role of bacteria in petroleum genesis; certain geologists believe bacterial activity is limited to an initial period before the source material is buried deeply (White, 1935), while others believe bacteria remain active during the entire process (McCoy and Keyte, 1934).

Emery (1939) developed a heavy gravity coring tube which is a greatly enlarged modification of the Ekman (1905) mud sampler. Through the cooperation of Dr. F. P. Shepard and Dr. R. Revelle several cores of considerable length, obtained with this instrument on cruises of the "E. W. Scripps" were made available for bacteriological analysis. The results of these analyses are the subject of the present paper.

EXPERIMENTAL

The coring device consists of three principal parts: an upper iron pipe on which 200 to 500 pounds of streamline lead weights are placed; a valve to prevent loss of the core; and a lower iron pipe two inches in diameter and six to twenty feet long, the length used depending on the type of sediment expected. A special nose used on the end of the lower pipe serves to decrease the frictional force between the inside of the core tube and the mud. This instrument has taken cores up to 370 centimeters in length and has been used successfully in water over 4000 meters deep. The apparatus has actually penetrated as much as 770 centimeters into the sediment, but because of frictional forces a smaller and smaller percentage of each succeeding layer is collected as the corer moves through the mud (Emery and Dietz, 1939). Consequently the depth of the sample below the surface of the core as used in the following discussion and tables does not represent the actual depth below the surface of the sediment *in situ*. The actual depth will be greater than that reported by an amount depending in part on the ratio of the length of penetration of the core barrel to the length of core recovered, and in part on the nature of the sediment itself.

Usually the sediment was removed from the core tube immediately after being brought on board the vessel and cut into three- to five-inch sections which were stored in glass-covered pint jars. Samples for bacteriological analysis were obtained by dissecting out a radially central portion of mud from the inside of the freshly cut sections, using aseptic technique during all manipulations. These sub-samples were stored in sterile tubes or bottles in a refrigerator at 0° C. until returning to the laboratory on shore where the analyses were made. Core F 72, however, was analyzed on board immediately after it was obtained.

Ten grams of the sediments were weighed into tared dilution bottles

containing 90 cc. of sterile sea water. The bottles were then shaken vigorously for at least five minutes to obtain a uniform suspension. One-cc. portions of appropriate dilutions of the suspension were used to inoculate Petri dishes to determine the aerobic population, and oval tubes (Rittenberg et al., 1937) to determine the anaerobic population. A 1 : 100 dilution was the lowest used in making aerobic counts. If no colonies developed on either plate inoculated with this dilution the count was recorded as <50. A nutrient medium of sea water plus 0.3 per cent bacto-peptone, 0.2 per cent each of proteose-peptone and beef extract, 0.025 per cent $FeCl_3 \cdot 6H_2O$, and 1.5 per cent agar at a pH of 8.0 was used. The inoculated plates and oval tubes were incubated at 20° C. for two to four weeks before the colonies were counted.

All the samples examined, with one exception, were terrigenous deposits (Murray and Renard, 1891). According to the system of classification in use at the Scripps Institution (Revelle, 1940) these sediments are green clays or silts. Their median particle diameters vary from core to core and within individual cores, ranging from 2.5 to 44 microns. Their water contents vary with depth of burial and particle size, ranging between 30 and 70 per cent. Their organic nitrogen content falls between .10 and .32 per cent. The one pelagic deposit examined, F 72, consists of red clay overlying a very fine, dry, gray-green clay. Its median diameter ranges from 2.5 to 3.5 microns.

Bacteriologically the nine terrigenous samples roughly fall into three groups characterized respectively by high, intermediate, and low bacterial populations. This classification does not give a sharp separation because certain of the cores might be placed in either of two groups, depending on the portion of the data stressed. The terms high and low populations refer only to the ranges observed in this investigation and are used merely for convenience in discussing the data; it should not be inferred they delimit the maximum and minimum possible bacterial contents of terrigenous sediments.

Table I shows the number of bacteria demonstrated at various levels in cores of green mud of intermediate population. The number of aerobes in the topmost layer is high, ranging between one million and eight million per gram wet weight. Immediately below the surface of the mud the number of bacteria found decreases rapidly, less than 10,000 per gram being present at a depth of 20 centimeters. Very few bacteria develop from sediment layers 70 centimeters or more below the surface, the number, with one exception, being below 500 per gram. A characteristic shown by FPS 149 which is common to almost every core examined is that at all levels the aerobes are more numerous than

the anaerobes. Only 1,500 anaerobes per gram were demonstrated at the surface of FPS 149; the number found dropping to less than 500 per gram in the first 30 centimeters and remaining very low throughout the rest of the core. It is unfortunate that the anaerobic populations of the other two cores were not determined.

Table II shows the vertical distribution of bacteria in two cores of green mud of low population. The cores in Table II are separated from those in Table I only because of the large differences in the aerobic population of the surface layers. In the deeper portions the numbers and vertical distribution of bacteria in the two groups of cores are quite similar.

The results of the counts on sediments of high population are given in Tables III and IV. In these cores the numbers of aerobes and anaerobes in both the surface and subsurface layers are considerably higher than in the cores discussed above. At the surface the counts are as much as tenfold greater and in the lower layers there are differences up to ten thousandfold. Core FPS 253 might have been included in the intermediate group but because of the large number of bacteria at the surface it is also considered a sediment of high population. It

TABLE I

NUMBER OF AEROBIC AND ANAEROBIC BACTERIA PER GRAM OF WET SEDIMENT DEMONSTRATED IN DIFFERENT STRATA OF CORES OF GREEN MUD OF INTERMEDIATE POPULATION

Sample	FPS 149		39-C-39		39-C-40A	
Location of station	32° 36.4′ N. 117° 27.8′ W.		33° 02.5′ N. 118° 01.5′ W.		33° 04.5′ N. 117° 55.5′ W.	
Depth overlying water	1190 meters		935 meters		916 meters	
Time stored before analysis	12 hours		4 hours		4 hours	
Depth of sample below surface of core in cm.	*Bacteria per gram* *aerobes*	*anaerobes*	*Depth of sample below surface of core in cm.*	*Bacteria per gram aerobes*	*Depth of sample below surface of core in cm.*	*Bacteria per gram aerobes*
0–2	7,500,000	1,500	0–3	1,850,000	0–2	2,415,000
2–5	250,000	2,250	3–8	230,000	2–5	55,000
5–9	200,000	7,200	8–18	2,900	5–8	15,800
9–13	100,000	1,350	18–28	600	10–12	800
18–22	20,000	470	48–58	<50	20–22	150
28–43	3,300	5	79–89	2,150	36–38	50
43–58	2,100	80	109–119	400	53–55	<50
58–74	100	10	137–150	50	74–76	400
74–89	200	10	170–180	250	91–94	<50
89–104	150	45				
104–119	150	10				
119–134	50	5				
134–149	100	5				
149–165	<50	0				
165–180	150	5				
180–196	200	5				

TABLE II

NUMBER OF AEROBIC AND ANAEROBIC BACTERIA DEMONSTRATED IN DIFFERENT STRATA OF CORES OF GREEN MUD OF LOW BACTERIAL POPULATION

Sample	39-C-1		39-C-4	
Location of station	32° 55.7′ N. 117° 36.8′ W.		33° 03.3′ N. 117° 25.5′ W.	
Depth overlying water	935 meters		465 meters	
Time stored before analysis	8 hours		6 hours	
Depth of sample below surface of core in cm.	*Bacteria per gram of sediment (wet weight) aerobes*	*anaerobes*	*Depth of sample below surface of core in cm.*	*Bacteria per gram of sediment (wet weight) aerobes*	*anaerobes*
0–5	180,000	7,500	0–3	240,000	17,500
5–17	60,000	6,500	3–8	155,000	12,000
30–43	1,100	30	33–46	300	10
56–69	50	0	71–76	350	65
81–94	100	0	109–122	50	0
145–158	<50	0			
185–198	<50	0			
211–224	100	0			
236–249	<50	0			

should be noted that the cores in this group were stored between 60 and 110 hours before analysis while those in the other two groups were all stored less than 12 hours.

Within certain cores the vertical distribution of bacteria departed from a general decrease in numbers with depth by a significant amount. In the two most striking examples observed (Table IV) the occurrence of layers of high population below layers of low population was associated with discontinuous changes in the physical properties of the sediment. In FPS 258, 270,000 bacteria per gram were found at a depth of 303–313 centimeters below the surface, while the number of bacteria in the layers above and below this depth was considerably

TABLE III

NUMBER OF AEROBIC AND ANAEROBIC BACTERIA DEMONSTRATED IN DIFFERENT STRATA OF CORES OF GREEN MUD OF HIGH BACTERIAL POPULATION

Sample	FPS 251		FPS 253	
Location of station	36° 13.0′ N. 121° 55.1′ W.		34° 49.0′ N. 121° 10.0′ W.	
Depth overlying water	676 meters		530 meters	
Time stored before analysis	108 hours		84 hours	
Depth of sample below surface of core in cm.	*Bacteria per gram of sediment (wet weight) aerobes*	*anaerobes*	*Depth of sample below surface of core in cm.*	*Bacteria per gram of sediment (wet weight) aerobes*	*anaerobes*
0–12	23,800,000	290,000	0–10	18,300,000	110,000
12–25	138,000	26,000	10–15	4,000	1,100
51–64	63,000	3,100	55–67	4,200	45
102–115	24,000	4,800	107–120	400	95
127–140	23,000	4,700	142–155	100	40

TABLE IV

NUMBER OF AEROBIC AND ANAEROBIC BACTERIA DEMONSTRATED IN DIFFERENT STRATA OF CORES OF GREEN MUD SHOWING ZONES OF HIGH POPULATION BENEATH ZONES OF LOW POPULATION

Sample	FPS 258		FPS 259	
Location of station	34° 14.0′ N. 120° 02.5′ W.		34° 11.8′ N. 120° 02.0′ W.	
Depth overlying water	566 meters		565 meters	
Time stored before analysis	60 hours		60 hours	
Depth of sample below surface of core in cm.	*Bacteria per gram of sediment (wet weight) aerobes*	*anaerobes*	*Depth of sample below surface of core in cm.*	*Bacteria per gram of sediment (wet weight) aerobes*	*anaerobes*
0–5	3,050,000	232,000	0–18	15,800,000	272,000
5–13	11,700,000	189,000	18–31	9,100,000	178,000
25–38	3,275,000	54,000	56–79	788,000	2,660
76–89	2,300,000	15,000	107–120	2,600	330
152–165	43,000	9,600	157–170	17,000	200
228–231	8,400	18,000	232–245	102,000	390
303–313	270,000	42,000			
342–355	15,000	2,200			

lower. A similar zone of high population was observed 232–245 centimeters below the surface in FPS 259. In exactly these same layers there was a very abrupt increase in the water content and decrease in the cohesiveness of the sediment. The zone of relatively high population at 78–89 centimeters depth in 39-C-39 has not as yet been correlated with an abrupt change in any other characteristic of the sediment.

Table V shows the numbers of bacteria found in the various layers of the only pelagic deposit examined. The numbers of aerobes and anaerobes were uniformly low throughout the length of the core with a maximum at the surface.

TABLE V

NUMBER OF AEROBIC AND ANAEROBIC BACTERIA DEMONSTRATED IN VARIOUS STRATA OF A CORE OF PELAGIC SEDIMENT

Sample	F 72	
Location of station	30° 25.0′ N. 118° 32.5′ W.	
Depth overlying water	3005 meters	
Depth of sample below surface of core in cm.	*Bacteria per gram of sediment (wet weight) aerobes*	*anaerobes*
0–5	3,300	600
28–36	200	100
66–74	300	100
104–112	600	100
142–150	350	100
180–188	600	450
218–226	200	200

DISCUSSION

The vertical distribution of bacteria in the upper sixty centimeters of the terrigenous deposits of clays and silts examined is very similar in certain general features to that reported by previous workers. The large population at the surface, the rapid decrease in numbers of bacteria with depth, and the larger number of aerobes than anaerobes found in most cores in this investigation have also been reported by Reuszer (1933), ZoBell and Anderson (1936) and others. However, there are great enough differences in the numbers and distribution of bacteria in the various cores examined to make one question the advisability of generalizing such data. Without discussing the specific factors which account for these differences, it can be said that they are due to extreme vertical and lateral variability in the bottom materials themselves. It follows that "average" distribution curves of bacteria are of value only when they apply to a well-defined, homogeneous sediment.

The bacterial population of the sediments buried under more than 60 centimeters is of special interest since no previous observations have been reported for these deeper layers. The data show that both aerobic and anaerobic bacteria are present at a considerable distance beneath the ocean floor. Even though cores as long as 355 centimeters were examined, a lower boundary of the bacterial population was not reached. The numbers of bacteria demonstrated in these lower levels was uniformly small in those samples analyzed immediately after collection. ZoBell (1938) has shown that the number of bacteria increase two- to fourfold after storage at 0° C. for 48 hours. The larger populations found in the samples stored for sixty hours or over may therefore be due in part to multiplication of bacteria after obtaining the core. Since only the stored cores showed high populations in the lower levels one might conclude that the populations *in situ* below 60 centimeters are always small. Only a small number of cores were examined, consequently this apparent relationship may be due to entirely different, unrecognized factors. The multiplication of bacteria in the sediments during storage shows that these muds are capable of supporting many more bacteria than are usually found, and it is possible that under certain circumstances the population *in situ* in deeply buried layers may approach that of the surface layer.

The small number of anaerobes found in the lower layers is quite puzzling. The green clays and silts contain an abundance of organic matter (Revelle and Shepard, 1939) and are very reducing in nature (ZoBell, 1935), often containing free hydrogen sulphide in the subsurface layers. These characteristics should all be conducive to an

abundant anaerobic microflora. Part of the reason for the paucity of anaerobes detected may lie in the method of making the counts, since the oval-tube procedure has the same limitations as any indirect method of enumerating bacteria based on the counting of colonies developing on a single medium. Very little information is available on the type of substrate best suited for growing the maximum number of a naturally-occurring mixed microflora of anaerobes. It is quite probable that the nutrient medium used in this investigation is not suitable for the bacteria existing on the relatively resistant organic compounds occurring in sediments which have been subjected to intensive aerobic and anaerobic decomposition.

The recovery of viable bacteria from deep layers of sediment is not proof of their activity in that material. It is well known that spores exist for long periods in a quiescent state and there is a growing belief that non-spore-forming bacteria may also have some type of resting stage. The isolation of aerobic, non-sporulating bacteria from the anaerobic environment of these sediments lends some support to this belief. As pointed out by ZoBell (1938), the small number of bacteria present in the lower layers may represent dormant survivals of the active population present when the sediment was first laid down. The opposite hypothesis, that most of the bacteria demonstrated are active *in situ*, and that the small numbers present (allowing for the limitations of the enumeration procedures) result from various unfavorable environmental conditions such as low temperature, low water content, and other inimical factors, seems equally probable.

The occurrence of discontinuous zones of bacterial populations in the same loci where there are abrupt changes in the physical and chemical properties of the sediments is a striking example of the relation between population and environment. It is of interest to point out that the observation of such biological zonation can serve to focus attention on changes in physical or chemical properties which might otherwise be overlooked.

Core F 72 is the only pelagic deposit represented in this series and to the best of the author's knowledge the data presented is the only report in the literature on the vertical distribution of bacteria in such sediments. The number of viable bacteria recovered from this material is much smaller than from the terrigenous deposits. Even though only one pelagic sample has been analyzed, it is believed that small bacterial populations will be characteristic of all such deposits. This conclusion is based on the very slow rate of deposition of these sediments, estimated to be less than a centimeter every thousand years, and on the correspondingly long period of oxidation undergone before the

material is buried beneath the ocean floor (Revelle, 1940). As a consequence most of the utilizable organic matter would be decomposed while the sediment was in contact with oxygen-bearing bottom water leaving very little for bacteria to multiply upon immediately below the surface of the deposit. It is hoped that more pelagic sediments will be available in the near future so that additional data can be gathered on this point.

SUMMARY

The numbers of aerobic and anaerobic bacteria present at various depths in cores of marine sediments up to 355 centimeters in length were determined.

Viable bacteria were found in the bottom of the longest cores examined although in most instances the number present was very small.

The numbers of bacteria found vary greatly from core to core at corresponding depths and also vertically in individual cores. A decrease in bacterial population with depth was usually observed. Many more aerobes than anaerobes were demonstrated even though conditions below the surface of the sediments appeared to be more favorable for anaerobic growth. The smaller number of anaerobes found may be partly due to limitations in the enumeration procedure.

In certain sediments, zones of high bacterial population were found beneath zones of low population. In two instances the location of such zones corresponded exactly with the loci of abrupt changes in other characteristics of the sediments.

The number of bacteria demonstrated in the one pelagic deposit examined was much smaller and more constant than in the terrigenous deposits.

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POTENTIAL VORTICITY AS A CONSERVATIVE PROPERTY

By

V. P. STARR AND M. NEIBURGER

The problem of tracing actual trajectories of air particles in the free atmosphere, and of water particles in the ocean, has been attacked for many years without a definitive solution. The introduction of the isentropic chart in meteorology a few years ago was a great forward step. Corresponding methods have also been applied to oceanography, and it is evident that any advancement made towards the solution of the problem of actual trajectories in either branch of the geophysical sciences must also contribute to its solution in the other field. In its general aspects the problem is therefore common to both meteorological and marine research. In the present article it will be discussed on the basis of its meteorological phase.

In its application to meteorological studies the method of the isentropic charts makes use of the fact that atmospheric motions over short time intervals are essentially adiabatic, i.e., conservative of potential temperature. The use of a second conservative element, the specific humidity or some function thereof, as a further identifying index, has made it possible to follow air currents in a general way, since a curve drawn for equal values of the specific humidity on a surface of constant potential temperature will remain an equisubstantial curve during processes for which these two elements are conserved. This means that if there is no change in heat or water vapor content by radiation, condensation or evaporation, and if there is no mixing, a particle which is on a line defined by a particular value of specific humidity on a given isentropic surface will be found somewhere on the line representing that specific humidity on the chart drawn for the same isentropic surface at a later time. If there were some means of selecting the particle along the line on the second chart which corresponds to a certain point on the first, the trajectories of the air particles could be traced, in so far as the motion satisfies the conditions under which the identifying elements are conserved.

The one means of discriminating between the elements of such an equisubstantial line is to have a third independent identifying element which is conserved by the air particle from time to time. Using it, it would be a simple matter to follow an air particle in a synoptic situation by constructing the isentropic charts for a particular potential

temperature, drawing the lines for constant values of specific humidity and our new identifying element, and finding the points on the successive charts representing the intersections of a particular specific humidity line with the line representing a certain value of the third element. In other words, the three conservative properties would constitute a Lagrangean coordinate system by which the motions of air particles could be followed.

Thus, our problem is reduced to that of finding a third conservative property of a parcel of air, independent of potential temperature and specific humidity, so that its isopleths will intersect the lines of constant specific humidity on an isentropic surface. To find such a property we must take stock of the quantities measured or measurable in the free atmosphere. By means of our radio soundings we measure pressure, temperature and relative humidity. By means of pilot balloons followed by theodolites we obtain the wind velocity at various heights. Regarding the pressure as an independent variable corresponding to height, we obtain the space-fields of temperature, relative humidity, and wind velocity by means of direct observation. It is obvious that none of these elements is conservative. We have already seen, however, that from the temperature and humidity observations may be derived quantities which are conservative, namely, potential temperature and specific humidity. Since no more than two independent functions of two variables exist, for a third function we must turn to the wind field as an additional variable.

Professor C. G. Rossby demonstrated some time ago a theorem which presents us with a function of the field of motion of certain types of fluids which is conserved. This theorem, which is an application of the equations of motion or the circulation theorem, has been published recently (*1*). The theorem is summarized by the equation

$$\frac{f + \zeta}{D} = \text{constant},$$

where $f = 2\Omega \sin L$ is the absolute vorticity of the earth's surface about a vertical axis at latitude L, ζ is the vertical component of the vorticity of the fluid relative to the earth's surface, and D is the depth of the fluid at the point. The theorem holds strictly either for a homogeneous incompressible fluid, or for an adiabatic layer of a compressible fluid. In the latter case D represents not the geometric depth, but the difference in pressure between the bottom and the top of the layer. Since a very thin layer in the free atmosphere may be considered to be characterized by a constant potential temperature, the theorem may be considered to hold approximately for such a layer.

Thus, we have found a property of the field of motion which is approximately conserved under certain restricted types of motion, the restrictions being exactly those for which both specific humidity and potential temperature are conserved. The quantity $\frac{f+\zeta}{D}$, however, has no immediate physical significance, and unusual dimensions. On the other hand, consider the quantity ζ_0, defined as that vorticity which a fluid column having an observed vorticity ζ and thickness D at a latitude where the Coriolis parameter has the value f, would obtain if it were brought to an arbitrary "standard" latitude where the Coriolis parameter is f_0, and then stretched or shrunk to the arbitrary "standard" thickness D_0. Then, if the motion is adiabatic and does not involve mixing,

$$\frac{f_0+\zeta_0}{D_0}=\frac{f+\zeta}{D}$$

and

$$\zeta_0=\frac{f+\zeta}{D/D_0}-f_0$$

The quantity ζ_0 thus is constant for all processes for which $\frac{f+\zeta}{D}$ is constant, and represents the vorticity which the column in question would have if brought to a standard latitude and thickness, just as the potential temperature is that temperature which an air parcel would attain if it were brought adiabatically to a standard pressure. By analogy we can call ζ_0 the *potential vorticity.*

For synoptic use it is desirable to obtain ζ_0 not merely for certain selected points, but to evaluate it over the entire isentropic chart, and represent it by isopleths in the same way as the specific humidity is represented.

Unfortunately the potential vorticity cannot be directly observed, nor is it a simple, easily computed function of directly observed quantities. In its evaluation enter the quantities f, D, and ζ. The Coriolis parameter f is, of course, constant for each particular latitude. The depth of the layer between two isentropic surfaces is measured at the radiosonde stations, and by careful construction of lines of equal depths the entire field may be closely approximated. The actual vorticity ζ, however, requires differentiation of the components of the wind velocity. It will be remembered that

$$\zeta=\frac{\partial v}{\partial x}-\frac{\partial u}{\partial y}$$

where u and v are the components of velocity along the x and y (horizontal) axes. Actually, because of the convergence of the meridians, if the y axis is taken toward the north there is another term, and the complete expression is

$$\zeta = \frac{\partial v}{\partial x} - \frac{\partial u}{\partial y} + \frac{u}{a} \tan L$$

where a is the radius of the earth, and L is the latitude. It is readily seen that the last term is small except in the polar regions, for below 60° tan $L<2$, and for $u = 10$ *m.p.s.*, $\frac{u}{a} = \frac{10}{3.18 \cdot 10^6} = 3 \cdot 10^{-6}$, and $\frac{u}{a} \tan L \sim 6 \cdot 10^{-6}$. The values of ζ vary from $5 \cdot 10^{-5}$ to $-5 \cdot 10^{-5}$, so that the neglect of the last term introduces no error of consequence in the region with which we are concerned.

In arriving at the field of actual vorticity, ζ, lines of equal values of u and v are drawn on separate Mercator charts on the basis of the observed winds at the level of the selected isentropic surface. The differentiation is performed by means of scales giving the shear in mps/100 km corresponding to various separations of the u-lines along the meridians and the v-lines along the parallels, respectively, different scales being necessary for each five degree zone because of the change of linear scale with latitude on the Mercator projection. Lines of equal values of $\frac{\partial u}{\partial y}$ and $\frac{\partial v}{\partial x}$ are drawn on the separate charts, and graphical subtraction of the first set of lines from the second gives ζ, the vorticity of the wind field.

To reduce this actual vorticity field to "standard" conditions, i.e., to obtain ζ_0, it is now necessary to add f, the field of which is represented by the parallels of latitudes L corresponding to unit values of $2\Omega \sin L$ expressed in the units 10^{-5} $\sec^{-1}$, and then to divide by the field of D/D_0. These operations may be performed graphically with the aid of an illuminated drawing board. The subtraction of f_0 corresponds merely to a relabelling of the lines resulting from the division, resulting finally in the lines of constant potential vorticity for the entire chart.

The computations involved are rather long although it is not inconceivable that the routine can be developed to the point where potential vorticity lines on the basis of the early morning aerological data may be included in the isentropic chart used in the morning forecast.

Theoretically, there is another method of obtaining the vorticity ζ. For strictly two dimensional flow there exists a stream function ψ, such that

$$u = -\frac{\partial \psi}{\partial y}, \qquad v = +\frac{\partial \psi}{\partial x}$$

If the stream lines defined by this function are plotted, ζ may be obtained very simply, for we have, by differentiating

$$\zeta = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2}$$

To obtain the vorticity at the point (x, y), we choose any convenient unit of length, and then, by finite differentiation we obtain the expression

$$\zeta = \psi(x + 1, y) + \psi(x - 1, y) + \psi(x, y + 1) + \psi(x, y - 1) - 4\psi(x, y)$$

Montgomery (*2*) has given an equation for what he calls the "isentropic geostrophic potential," namely

$$\psi_1 = c_p T + gz$$

such that

$$u_1 = -\frac{1}{f}\frac{\partial \psi_1}{\partial y}, \quad v_1 = \frac{1}{f}\frac{\partial \psi_1}{\partial x}$$

where u_1 and v_1 are the components of the geostrophic wind. Using these expressions and neglecting the variations in f,

$$\zeta = \frac{1}{f}\left(\frac{\partial^2 \psi_1}{\partial x^2} + \frac{\partial^2 \psi_1}{\partial y^2}\right)$$

A good approximation of the vorticity may be obtained by using this function, and it is desirable to use it in those regions where cloudiness prevents the observation of the actual winds.

The network formed by the potential vorticity lines and the specific humidity lines forms a coordinate system by which each column in the isentropic layer is labelled. If there is no mixing or non-adiabatic process during the period between two consecutive charts, on the second chart each fluid column will be characterized by the same coordinates as the first. While there may be more than one intersection of a particular potential vorticity line with a selected specific humidity line, the corresponding ones on successive maps may be determined easily from a consideration of the wind field. A fluid column having particular values of ζ_0 and q on one map must be identified not merely by the fact that it still has these values, but also that the wind in the interval between maps was that which would bring the fluid column into its new position.

By carefully identifying the columns on the successive maps, using the six-hourly wind field in rapidly changing situations, the actual trajectories of the fluid columns may be plotted throughout a synoptic situation, except in so far as the motion is affected by non-adiabatic processes and mixing. This procedure, it is hoped, will lead to an increase in our knowledge of the behavior of the currents in the isen-

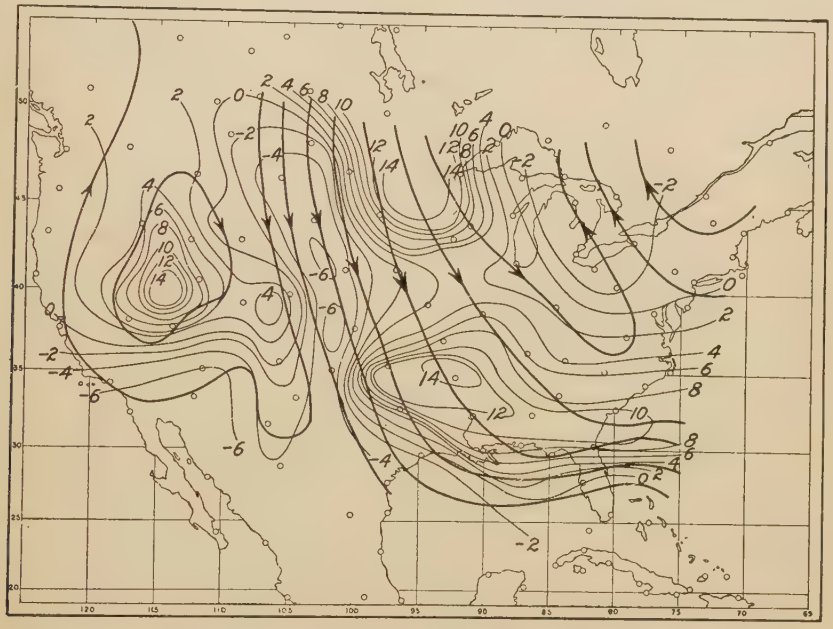

Figure 53. Potential vorticity lines (thin lines) and stream lines (thick lines with arrows), Nov. 21, 1939.

tropic chart. Such questions as the conditions under which upslope motion of the currents of moist air occur may be investigated by this means.

In addition to its value as a research tool in investigating past weather, the use of potential vorticity gives promise of being of prognostic worth. The transport of potential vorticity affects the windfield, and may become useful in predicting changes in it. This aspect of the problem has only been speculated upon so far. It is hoped that a later study will establish definite results in this direction.

Another use to which the concept of potential vorticity may be put is the investigation of non-isentropic processes. For instance, the

question of whether a given circulation is produced thermally or dynamically may be answered by considering whether or not ζ_0 has been conserved in the currents involved.

In the various applications suggested it will be necessary to construct charts for more than one thin layer in order that the entire vertical extent of the atmosphere be considered. We have confined the present investigation primarily to developing the technique of con-

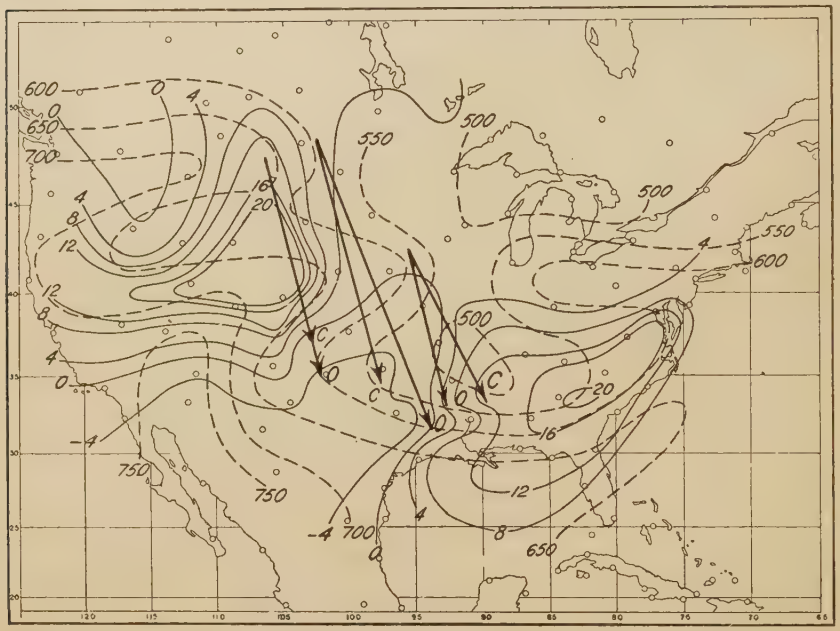

Figure 54. Potential vorticity lines (solid) and isentropic condensation isobars (broken), Nov. 22, 1939.

structing charts of potential vorticity and to testing whether the fluid columns appear to conserve this quantity in one isentropic layer.

The potential vorticity field for the layer $\theta = 299°$ to $\theta = 303°$ on November 21, 1939 is represented, together with the stream lines, in Figure 53. It is seen that ζ_0 has maxima in the Mississippi Valley and over the Great Basin, and a minimum just east of the Rockies. The distribution of ζ_0 on the following day is shown by the solid lines in Figure 54. While the values of the maxima have changed, their positions have been displaced in a direction and with a velocity which is in complete accord with the lines of flow on Figure 53. The center

over Arkansas has followed the stream lines to Georgia, and that east of the Rockies has moved with the current to Texas. Thus, the general movement of the field of vorticity appears to be that of the air currents of the layer.

In Figure 55 the lines of potential vorticity and specific humidity for November 21 are shown together. The intersections of these lines should identify fluid particles. The origins of the arrows in Figure 54 are the positions of three such intersections. The heads marked *C* are

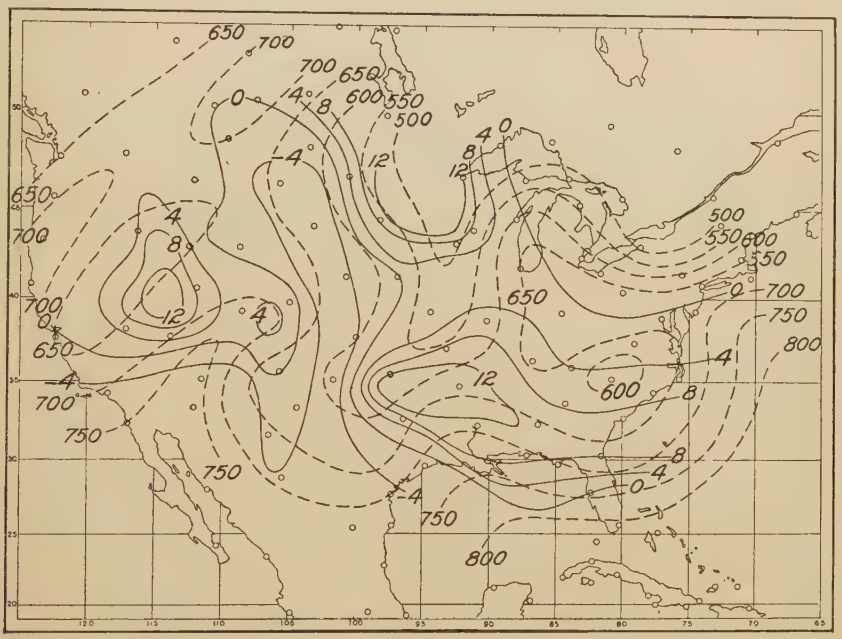

Figure 55. Potential vorticity lines and isentropic condensation isobars. Nov. 21, 1939.

obtained by projecting the wind velocity in the direction of flow for 24 hours. Thus they indicate the positions the selected intersections would reach if they moved with the wind observed at the time for the next 24 hours. The heads marked *O* are the positions characterized by the intersections of the same q and ζ_0 lines 24 hours later. The observed positions in all three cases correspond very closely with those computed by simple extrapolation, and provide a remarkable check on the conservatism of potential vorticity, especially in view of the crude method of computation.

The apparent change in the magnitude of the maximum in the Southeast may be false, as the wind field was interpolated there. That over the Great Basin, on the other hand, is due to non-adiabatic processes, as the layer was close to the ground there.

This preliminary investigation thus indicates that potential vorticity is a conservative property of air columns, and may be used to trace trajectories in the free atmosphere. Further studies concerning its usefulness in studying non-adiabatic processes, mixing, and prediction of the upper air winds are contemplated.

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THE EFFECT OF OXYGEN TENSION ON THE RATE OF OXIDATION OF ORGANIC MATTER IN SEA WATER BY BACTERIA[1]

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It is generally recognized that the oxygen consuming capacity of heterotrophic bacteria in water serves as a good criterion of the amount of respirable or oxidizable organic matter in the water. However, the fragmentary literature on the subject records contradictory observations on the effect of oxygen tension upon the rate of bacterial oxidations. For example, Pomeroy (1938) found the amount of oxygen consumed by diluted sewage containing from 0.7 to 17.5 cc. of oxygen per liter to be independent of the oxygen tension but Heukelekian (1936) noted the maximum consumption of oxygen in such sewage mixtures containing around 10.5 cc. of oxygen per liter. According to Waksman and Carey (1935a) organic matter in sea water is oxidized more and more slowly as the oxygen tension is reduced. Conversely ZoBell and Stadler (1940a) report that the rate of bacterial oxidation of organic matter in lake water is not influenced by the oxygen tension within the examined ranges of 0.21 to 25.5 cc. of oxygen per liter.

In order to standardize procedures for the determination of the respirable organic matter content of sea water as well as to estimate the amount of oxygen being consumed by bacteria *in situ* it is necessary to have information on the effect of oxygen tension on bacterial respiration. The far-reaching significance of such determinations is emphasized by Sverdrup (1938) who points out that a rational explanation of the distribution of oxygen is the oceans awaits information on the "amount of oxygen-consuming organic matter" at different depths and the effect of oxygen content of the water on oxygen consumption.

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EXPERIMENTAL

Sea water was collected in 5-gallon carboys from Buzzards Bay or Vineyard Sound and brought into the laboratory. It was filtered through No. 25 bolting silk and thoroughly shaken to insure uniformity in its bacterial and chemical composition. The water was warmed to 22° C. and distributed in 4 l. quantities in gallon bottles. Tank nitrogen, or oxygen as required, was bubbled through the water until the dissolved oxygen of the water was adjusted to the desired concentration. By using flow meters it became possible to admit almost exactly the required amount of nitrogen or oxygen. The water was siphoned into 140 ml. glass-stoppered bottles under an atmosphere of nitrogen and oxygen which was in equilibrium with the partial gas pressure of the water being bottled. The oxygen content of the first two bottles filled with water and the last two was determined at once, these being used as controls to show the initial dissolved oxygen content of the water. The remaining bottles of water were placed in a water bath at 22° C. and the oxygen content determined after different periods of incubation.

The oxygen tension of the water was determined by the Winkler technique (Thompson and Robinson, 1939) using a microburette and N/100 sodium thiosulphate for titrations. In most cases the initial quadruplicate determinations agreed to within 0.03 cc./l. and the series was discarded if the divergence of duplicates exceeded 0.10 cc./l.

The bottles, siphons and other glassware used in the experiments were cleaned with sulphuric-acid dichromate solution and thoroughly rinsed. These precautions were exercised because of the known tendency of organic matter and bacteria to accumulate on glass immersed in water (Stark et al., 1938).

Adjusting the oxygen tension of sea water by the procedures outlined above has a slight effect on the carbon dioxide tension and may alter other properties of the water but the following experiment demonstrated that neither the rate nor the amount of oxygen-consumption was influenced by such treatment. Part of a sample of sea water was transferred to each of several glass-stoppered bottles without treatment. The oxygen tension of the second portion of the water sample was reduced to 0.64 cc./l. by bubbling nitrogen through it. Part of this was then bottled and to the remainder oxygen was admitted until it approximated the oxygen content of the original sample. Oxygen was bubbled through another portion of the water sample until it contained 12.74 cc./l. Part of this was bottled and to the remainder nitrogen was admitted until the oxygen tension was reduced to approximately that of the original sample after which it was bottled. Duplicate

bottles of water receiving each treatment were analyzed after different periods of incubation in the water bath at 22° C. The results which are summarized in Table I show that within the limits of experimental error the same amount of oxygen is consumed by the respiring bacteria in sea water regardless of the treatment of the samples with nitrogen or oxygen.

The effect of oxygen tension on the rate of bacterial respiration in sea water was studied by adjusting the oxygen tension of different lots of a large sample of water collected from Buzzards Bay (6/23/39) at concentrations ranging from 0.41 to 18.04 cc./l. by treating with either

TABLE I

Oxygen Consumed After Different Periods of Time at 22° C. by Bacteria in Sea Water the Gas Tension of Which Had Been Altered by Bubbling Either Nitrogen or Oxygen or Both Gases Alternately Through the Water

Gaseous treatment	*Initial dissolved oxygen*	*Oxygen consumed after* 2 days	5 days	10 days	20 days
	cc./l.	cc./l.	cc./l.	cc./l.	cc./l.
None	5.46	0.24	0.39	0.87	1.26
Nitrogen	0.64	0.25	0.34	0.62	—
Nitrogen + oxygen	5.72	0.28	0.43	0.95	1.21
Oxygen	12.74	0.21	0.41	0.97	1.32
Oxygen + nitrogen	5.30	0.25	0.36	0.84	1.24

nitrogen or oxygen. Quadruplicates were analyzed for oxygen content at once and duplicates after different periods of incubation in the water bath at 22° C. Prior to the addition of the Winkler reagents 1.0 cc. of water from each bottle was withdrawn for estimating the bacterial populations. Appropriate dilutions were plated with nutrient sea water agar and the colonies were counted after 10 days incubation at room temperature. From these data the amount of oxygen consumed per bacterial cell was calculated by applying the formula of Buchanan and Fulmer (1930): $m = \frac{2.303\, S \log b/B}{t(b - B)}$, where m is the amount of oxygen consumed per cell per hour, S the total amount of oxygen consumed in time t, B the number of bacteria at the beginning of the experiment and b the number after time t. Table II records the amount of oxygen which was consumed by the bacteria after different periods of incubation in water containing different concentrations of oxygen and the amount of oxygen which was consumed per cell per hour during the first two days of the experiment. Although all of the requisite conditions do not prevail to make the application of the

formula of Buchanan and Fulmer strictly valid, it is noteworthy that for each oxygen tension the rate of respiration of the bacteria is found to be of the same order of magnitude.

The rate of oxygen consumption was virtually the same for water of all oxygen concentrations until the concentration of oxygen was reduced to less than 0.2 cc./l. The rate of oxygen consumption decreased after two days incubation at 22° C. Excluding the first two series in Table II which initially contained the least dissolved oxygen and in which the

TABLE II

Oxygen Consumed by Multiplying Bacteria in Sea Water Containing Different Concentrations of Dissolved Oxygen at 22° C. and the Amount of Oxygen Consumed Per Cell Per Hour During the First Two Days of the Experiment as Calculated from Data on the Bacterial Populations and the Oxygen Tension

Initial dissolved oxygen	*Oxygen consumed after*				*Oxygen consumed per cell per hour during first two days*
	1 day	*2 days*	*5 days*	*10 days*	
cc./l.	cc./l.	cc./l.	cc./l.	cc./l.	cc.
0.41	0.07	0.20	0.37	0.39	13.9×10^{-12}
0.77	0.06	0.24	0.55	0.72	9.2×10^{-12}
1.19	0.06	0.21	0.62	0.95	12.5×10^{-12}
2.36	0.08	0.26	0.56	0.91	16.1×10^{-12}
5.10	0.07	0.28	0.59	0.98	15.0×10^{-12}
8.26	0.09	0.25	0.61	0.92	14.3×10^{-12}
12.74	0.05	0.23	0.67	0.91	16.4×10^{-12}

total oxygen consumption was limited after two to five days by the amount of oxygen present, the bacteria consumed an average of 14.9×10^{-12} cc. of oxygen per cell per hour during the first two days of the experiment. The average rate had dropped to 9.5×10^{-12} cc. per cell per hour for five days and to 4.7×10^{-12} cc. for ten days. In fact, from the fifth to the tenth day of the experiment the bacteria were consuming an average of only 2.6×10^{-12} cc. of oxygen per cell per hour. The decreasing respiratory rate is attributed to the progressive utilization of the more readily oxidizable fractions of organic matter occurring in the sea water, although it may also be influenced by the age of the cells. It has been shown by Clifton and Logan (1939) and others that young cells in the logarithmic phase of growth use more oxygen than older cells. The tendency of the bacteria to adhere tenaciously to the glass walls of the bottle causing many respiring bacteria to escape detection by plating procedures is another complicating factor (ZoBell, 1936). For this reason the rate of respiration

after several days incubation may be considerably less than 2.6×10^{-12} cc. per cell per hour as estimated because there are probably as many or even more respiring bacteria which are tenaciously attached to the walls of the glass bottles than the number which are detected in the water by the conventional plate count procedure.

The enrichment of sea water with readily oxidizable substances accelerates the rate of oxygen consumption by bacteria. As has been shown by Waksman and Carey (1935b) the addition of utilizable organic matter to sea water causes a large increase in the bacterial population and oxygen consumption. According to Johnson (1936) the enrichment of sea water with 0.04 per cent of glucose increased the rate of respiration of marine bacteria 10 to 378 per cent. Similar results have been reported by ZoBell (1940) for both "resting" cells and multiplying cultures from lake water. In order to ascertain if the effect of oxygen tension on the rate of oxidation of organic matter is more pronounced in the presence of larger concentrations of readily utilizable organic matter, sea water was enriched with 0.05 per cent each of glucose and asparagine. The water was inoculated with mixed cultures of marine bacteria to give an initial bacterial population of approximately two million viable cells per cc. and the oxygen tension of different lots of the water was adjusted to range from 0.48 to 7.43 cc./l. The oxygen content of the water was determined from hour to hour and the amount of oxygen consumed was calculated. The results which are summarized in Table III show that the oxygen tension has

TABLE III

Effect of Oxygen Tension on the Oxygen Uptake of Bacteria in Sea Water Enriched with 0.05 Per Cent Each of Glucose and Asparagine

Initial	*Oxygen consumed after*				
dissolved oxygen	*2 hours*	*4 hours*	*6 hours*	*10 hours*	*16 hours*
cc./l.	cc./l.	cc./l.	cc./l.	cc./l.	cc./l.
0.48	0.05	0.15	0.31	0.48	0.48
1.14	0.06	0.14	0.34	0.91	1.14
1.97	0.07	0.18	0.38	1.01	1.46
4.15	0.04	0.12	0.35	0.95	1.53
7.43	0.03	0.17	0.40	1.04	1.61

no influence on the rate of respiration of bacteria in sea water enriched with organic matter until the oxygen tension is reduced to a very low level.

Waksman and Renn (1936) suggest that the effect of oxygen tension may be more pronounced when refractory substrates are being oxidized.

Therefore the experiment was repeated using aged sea water enriched with 0.05 per cent of ferric lignoprotein, a compound which is not readily oxidized by bacteria. The lignoprotein was obtained from Dr. Waksman. The "aged" sea water had been stored in the laboratory for several weeks to permit bacterial activity to oxidize the respirable organic matter. Controls run with this water revealed that it consumed only 0.26 cc. of oxygen per liter in 20 days at 22° C. The lignoprotein was slowly oxidized by the bacteria as indicated by bacterial multiplication and oxygen consumption but the rate of oxidation was found to be independent of the oxygen tension within the examined range of 0.41 to 8.93 cc. of oxygen per liter. The results of the experiment which has been repeated with similar findings are presented in Table IV.

TABLE IV

Effect of Oxygen Tension on the Oxygen Uptake of Bacteria Incubated at 22° C. in Aged Sea Water Enriched with 0.05 Per Cent of Ferric Lignoprotein

Initial	*Oxygen consumed after*				
dissolved oxygen	*1 day*	*2 days*	*3 days*	*5 days*	*10 days*
cc./l.	cc./l.	cc./l.	cc./l.	cc./l.	cc./l.
0.42	0.30	0.41	—	—	—
0.99	0.37	0.61	0.82	0.92	—
2.00	0.39	0.70	0.87	1.21	1.54
4.76	0.37	0.58	0.80	1.04	1.53
8.93	0.34	0.59	0.76	0.96	1.34

The lignoprotein was oxidized much more slowly than glucose or asparagine. A sample of isolated lignin purified by Bartlett and Norman (1938) was also found to be slowly oxidized by bacteria in sea water. From water enriched with 0.05 per cent of the lignin and which initially contained 0.78, 2.19, 5.30 and 9.04 cc. of oxygen per liter there was consumed an average of 0.54, 0.65, 0.57 and 0.61 cc. of oxygen respectively in 58 days at 22° C. ZoBell and Stadler (1940b) found that each of eleven different samples of purified or isolated lignins was slowly oxidized by bacteria in lake water and the rate of oxidation was independent of the oxygen tension until the latter was reduced to less than 0.3 cc. of oxygen per liter.

Waksman and Renn (1936) showed that the filtration of sea water removes an appreciable quantity of the oxygen consuming constituents and in so doing the effect of oxygen tension on the rate of oxygen consumption is amplified. The former observation has been confirmed by testing the oxygen consuming capacity of sea water treated in different

ways. Large samples of surface water were divided into three lots. The first was siphoned into glass-stoppered bottles without any treatment. The second lot was filtered through No. 25 bolting silk and then bottled. The third lot was filtered through a No. 4 sintered-glass filter and shaken to equilibrate it with air after which it was bottled. An unfiltered sample of surface water collected from Buzzards Bay (6/24/39) was found to consume 0.86 cc. of oxygen per liter in 20 days at 22° C. That which was filtered through bolting silk consumed 0.60 cc. of oxygen per liter while the sintered-glass filtered water consumed only 0.49 cc. of oxygen per liter. Unfiltered, silk-filtered and sintered-glass filtered water collected from Vineyard Sound (8/4/39) consumed 1.09, 0.75 and 0.53 cc. of oxygen per liter respectively in 20 days at 22° C.

Using the method suggested by Dr. C. E. Renn a large volume of sintered-glass filtered sea water was obtained by immersing 2-liter bottles fitted with No. 4 sintered-glass filters to a depth of ten or twelve fathoms where the hydrostatic pressure forced water into the bottles. This water from which much of the particulate and readily utilizable organic matter had been removed by the filters was tested for its oxygen consuming capacity in the presence of different concentration of dissolved oxygen. The oxygen tension of aliquot parts of the water was adjusted at different levels ranging from 0.49 to 9.05 cc./l. and the amount of oxygen consumed after different periods of incubation at 22° C. was determined. Corroborating previous findings it was found that the rate of oxygen consumption was appreciably slower in the sintered-glass filtered water than in unfiltered water collected from the same station and secondly, it was found that regardless of the more refractory characteristic and smaller concentration of the organic matter in the sintered-glass filtered water, the rate of oxidation

TABLE V

Effect of Oxygen Tension on the Oxygen Uptake of Bacteria in Sea Water Incubated at 22° C. Which Had Been Filtered *in situ* Through a No. 4 Sintered-Glass Filter

Initial dissolved oxygen	*Oxygen consumed after* 2 days	5 days	10 days	20 days
cc./l.	cc./l.	cc./l.	cc./l.	cc./l.
0.49	0.09	0.28	0.37	0.46
0.94	0.12	0.25	0.45	0.61
1.87	0.08	0.32	0.51	0.59
3.70	0.08	0.29	0.46	0.64
5.24	0.10	0.28	0.52	0.70
9.05	0.11	0.30	0.49	0.58

of the organic matter was independent of the oxygen tension over a wide range. The results are summarized in Table V.

In the foregoing experiments it was noted that the rate at which bacteria oxidize organic matter is not influenced by the oxygen tension of sea water until the latter is reduced to 0.2 to 0.3 cc. of oxygen per liter (see Tables II and V). Below this concentration of dissolved oxygen the rate of oxygen consumption decreases with decreasing oxygen tension. However, when corrections were made for the minute amounts of oxygen introduced by the Winkler reagents it was found that respiring bacteria are able to remove the last detectable trace of oxygen from sea water provided other conditions including utilizable organic matter do not become limiting factors.

DISCUSSION

The rate of oxidation of organic matter by bacteria in sea water does not seem to be influenced by the concentration of oxygen within the examined range of 0.3 to 12.74 cc./l. although it is influenced by the concentration of oxidizable organic matter. Apparently dissolved oxygen in sea water becomes a limiting factor in the bacterial oxidation of organic matter only when the concentration of oxygen is reduced to less than 0.3 cc. per liter. However, oxygen might become a limiting factor in localized microspheres rich in oxidizable matter such as, for example, the bodies of decomposing plankton organisms, if oxygen is consumed more rapidly than it can be replaced by diffusion from the surrounding water. Under these conditions a high oxygen tension in the surrounding water might be beneficial because it would increase the oxygen gradient and hence expedite the diffusion of oxygen to the oxygen-deficient microsphere.

According to Rashevsky (1933) the rate of oxygen consumption by protoplasm is independent of the oxygen tension except in so far as the latter might influence the diffusion or penetration rate of oxygen. Similarly Shoup (1929) concludes that "a constant and maximum rate of oxygen consumption occurs in small cells when the oxygen concentration becomes sufficient to entirely saturate the surface of the oxidative catalyst of the cell." He found that light production by photogenic bacteria, an oxidative reaction, was not dimmed until the oxygen was reduced to less than 0.1 cc. per liter.

Although most workers (Amberson, 1928, Harvey, 1928, Hyman, 1929, Shapiro, 1934, ZoBell and Stadler, 1940a) find that the respiratory rate of aquatic unicellular organisms is independent of oxygen tension over a wide range, there seem to be certain exceptions. Different bacteria may have different types of respiratory metabolism as

indicated by Schlayer's (1936) observation that 20 to 30 per cent of oxygen is optimum for the respiration of *Pneumococci* while the respiration of certain other bacteria he studied is unaffected by the concentration of oxygen until the latter is reduced to less than one per cent (about 0.2 cc. per liter). The difference may be related to the membrane permeability of the bacteria or it might be related to the e.m.f. or other peculiarities of the biological system. It is noteworthy that certain bacteria whose respiration is reported to be favored by a high concentration of oxygen, namely, *Pneumococci* (Schlayer, 1936), *Azotobacter* (Burk, 1930) and *Rhizobia* (Georgi and Wilson, 1933), are surrounded by capsular membranes which might tend to retard the diffusion of oxygen. Taylor (1935) has shown that there is a relationship between the respiratory rate and the e.m.f. of certain cells, and the e.m.f. in turn is influenced by the oxygen tension. Kempner (1937) reports that at low temperatures or with old cells the respiration of *Escherichia coli* is independent of the oxygen tension, but near the optimum temperature or with young cells the rate of respiration is a function of the oxygen tension.

The observations reported above as well as the work of Waksman and associates show that the concentration as well as the quality of the organic matter influences the rate at which it is oxidized. In general, the rate of bacterial respiration increases as the concentration of oxidizable organic matter increases but additional experiments must ascertain the range within which this generalization maintains. Working with lake bacteria ZoBell (1940) found that the optimum concentration of glucose for the respiration of lake bacteria was between 100 and 1000 mgm./l. and similar results were obtained with glycerol, asparagine and lactic acid. With this concentration of organic matter the rate of bacterial respiration independent of the favorable influence on bacterial multiplication was appreciably faster than in the presence of only 5 to 10 mgm. of organic matter per liter, the concentration which occurs in sea water. Considering that most of the organic content of sea water is highly refractory to bacterial oxidation, it appears that the concentration of organic matter is near the threshold of the requirements for bacteria which probably accounts for the paucity of bacteria in the ocean. There is no direct evidence that a lack of either utilizable nitrogen or phosphorus limits bacterial activity in the ocean although it has been demonstrated by Waksman and Carey (1935b) and Waksman and Renn (1936) that nitrogen limits bacterial activity when glucose is added to sea water.

Whereas the bacteria in sea water incubated at 22° C. consumed only 14.9×10^{-12} cc. of oxygen per cell per hour, they consumed

nearly four times as much or 54.1×10^{-12} cc. of oxygen per cell per hour at this temperature when the sea water was enriched with 0.05 per cent each of asparagine and glucose. Considering that the bacteria approximate spheres having a mean diameter of 1.0 μ and a density near that of sea water, it is estimated that in the sea they use about 30 cc. of oxygen per hour per gram of living cells and nearly four times as much (around 110 cc. per hour per gram) in the presence of an abundance of oxidizable organic matter. Heilbrunn (1937) has compiled data which show that various marine animals consume only from 0.002 to around 1.0 cc. of oxygen per hour per gram of fresh living material under comparable conditions. However, in spite of the relatively large oxygen consuming capacity of respiring bacteria, it would require a bacterial population of more than seven thousand per cc. to consume 1.00 cc. of oxygen from a liter of sea water in a year at 22° C., and proportionately more at lower temperatures. According to Johnson (1936) the Q_{10} of marine bacteria is 2.3 between 5° and 15° C. and 2.18 between 15° and 25° C.

If the results of this paper are applicable to conditions in the ocean, they have an important bearing on the explanation of the distribution of dissolved oxygen. It follows that where the concentration of oxygen is more than 0.3 cc./l. there exists no relation between the amount of oxygen consumed by bacteria and the amount present. Assuming that the bacterial oxidation of organic matter is the principal cause of oxygen consumption at depths well below the photosynthetic zone, say below 300 meters, no conclusions can be drawn concerning the rate of oxygen consumption from observations on the amount of oxygen present or vice versa because the two quantities are independent of each other. This is contrary to Sverdrup's (1938) suggested explanation of the oxygen minimum in the ocean. However, in fairness it should be added that Sverdrup emphasized the speculative character of his suggestion which was made to arouse interest in the problem. Moreover, at that time upon being consulted the author expressed the opinion that judging from reports in the literature, oxygen consumption by marine bacteria might be directly proportional to the oxygen tension, an opinion which is contradicted by the present findings.

Going a step further it appears that the distribution of oxygen in the ocean cannot be explained by considering only processes *in situ* but it is also necessary as Seiwell (1937) has done to consider the "history" of the water masses. In order to do so properly the factors which influence oxygen consumption must be studied further.

SUMMARY

The rate of oxidation of organic matter in sea water as indicated by oxygen consumption by bacteria is independent of the oxygen tension within the examined range of 0.31 to 12.74 cc. of oxygen per liter.

As the concentration of oxygen is reduced below 0.3 cc. per liter the respiratory rate decreases, although if oxidizable organic matter is present bacteria can remove the last detectable trace of dissolved oxygen from sea water.

During the first two days of incubation at 22° C. bacteria in sea water were found to consume an average of 14.9×10^{-12} cc. of oxygen per cell per hour; progressively less thereafter as the more readily oxidizable fractions of organic matter were utilized.

Although the enrichment of sea water with 0.05 per cent each of glucose and asparagine accelerates the rate of respiration, the rate in the enriched sea water is not influenced by the oxygen tension within the stated limits.

Filtering sea water through silk plankton netting or sintered-glass removes much of the more readily oxidizable matter from sea water but the rate of oxygen consumption by bacteria in the filtered water is independent of the oxygen tension.

Lignoprotein as well as a sample of purified lignin was found to be slowly oxidized by marine bacteria, the rate being independent of the oxygen tension.

The probable rôle of bacteria in influencing the distribution of dissolved oxygen in the sea is discussed.

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THE DETERMINATION OF THE ALKALINITY OF SEA WATER

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INTRODUCTION

In a previous paper one of us (*3*) described a method for the determination of the alkalinity of sea water—then termed the buffer capacity of sea water. This method was very rapid, eliminated the need for a titration process, and was particularly advantageous when working under rigorous field conditions. However considerable difficulty was sometimes experienced in the preparation of color comparison standards from base-free sea water. The method was later improved by Mitchell and Rakestraw (*2*). The present paper deals with a modification of the original method. The glass electrode is used for the measurement of excess acid and gives a precision greater than that obtained with color standards. If suitable shelter is available the method may be performed as readily in the field as in the laboratory. Following is a description of the apparatus and the method used.

DESCRIPTION OF APPARATUS

Potentiometer

A Leeds and Northrup pH potentiometer assembly was installed in the laboratory aboard ship in such a manner that it could be readily stowed when not in use. It was securely blocked and padded with sponge rubber and rested on cushions of the same material. The cushions aid in nullifying any vibrations that might affect the instrument.

The apparatus worked perfectly while the ship was under way and in moderate weather. In heavy swells the galvanometer needle oscillated slightly but by taking the midpoint of successive swings, as in making a weighing with an analytical balance, satisfactory results were obtained.

Automatic Pipets

A pair of 25 ml. automatic pipets made by Machlett and Son of New York was used to marked advantage in the measurement of the

standard acid (Fig. 56, *Left*). They were more rapid than the common type of pipet and markedly reduced potential personal errors

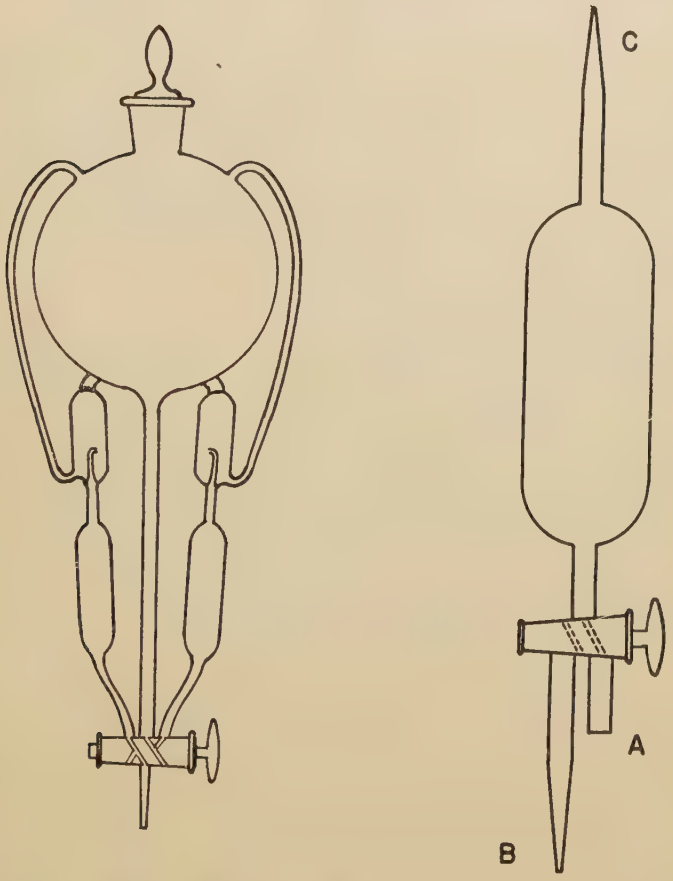

Figure 56. *Left:* Automatic pipet used for measuring the standard hydrochloric acid. *Right:* Sampling pipet. The pipet is filled by gravity from the water sampling bottle by means of a rubber tube connected at A. The pipet is filled partially after thorough rinsing. The stopcock is then turned so as to fill the tip B. When this has been done the stopcock is again turned and the pipet filled completely through A. This being done the sample is drained through B into the 135 ml. glass-stoppered bottle.

when a number of determinations were being made under rather adverse conditions. The pipets were adjusted and calibrated so that the delivery of the two did not vary by more than 0.02 ml.

Sampling Pipet

It is important that the sample of sea water for the determination be secured from the sampling device as soon as practicable after its arrival on board. A sample of water may be taken with a 100 ml. graduated cylinder, providing the method of manipulation is the same for all samples. If ample water is available a supply may be taken in a suitable container and the sample pipetted immediately in the usual manner. However it has been found to be more expedient to use a pipet of the type shown in Figure 56, *Right*. Its use permits direct sampling from the water bottle sampler, conserves the supply of the water sample, insures an accurate measure when the boat is not on even keel, and reduces errors due to loss or gain of carbon dioxide.

Calibration of Glass Electrodes

The glass electrode assembly was calibrated by using a potassium acid phthalate buffer having a pH of 4.0. The potassium acid phthalate is kept as a stock solution having a molarity of 0.2. For use this is diluted in order to secure a solution having a molarity of 0.05.

To facilitate the introduction of the samples and to speed up the measurements, the electrode assembly was provided with a funnel sealed to a glass delivery tube. This was placed so that the sample as it flowed into the cup rinsed the electrodes.

The sample cup was equipped with a stop cock so the sample could be drained readily without removing the cup from the electrode assembly.

PREPARATION OF REAGENTS

Hydrochloric Acid, 0.1000 N

A supply of exactly 0.1000 N HCl is prepared and standardized by potentiometric titration, using the glass electrode in conjunction with the extension lead assembly made by Leeds and Northrup. The acid may also be standardized against pure anhydrous sodium carbonate, using methyl orange as an indicator.

Hydrochloric Acid, 0.0100 N

The 0.1000 N hydrochloric acid is prepared as described above and then aliquots of this solution are diluted to exactly 0.0100 N, preferably in 10-liter quantities. The latter solution is not standardized by titration.

PROCEDURE

25 ml. of 0.0100 N HCl are pipetted into a dry 135 ml.–150 ml. glass-stoppered bottle. (If the sample bottle has been used in a previous

determination for alkalinity, its contents are drained and the standard hydrochloric acid is then introduced for the next determination. Rinsing with distilled water should be avoided because of the dilution effect, drying of the sample bottle then being essential.) 100 ml. of the sea water sample are added and the resulting solution thoroughly mixed by shaking. After coming to the temperature of the laboratory, a portion of the solution is used to thoroughly rinse the cup of the potentiometer in which the glass electrode is suspended. The cup is finally filled with the solution and the pH determined

The alkalinity of the solution is expressed by the number of milligram atoms of hydrogen ions (millimols or millequivalents) that react with the anions in the sea water. This may be calculated from the following:

$$\mathrm{pH} = \log 1 - \log [\mathrm{H}^+] \tag{1}$$

$$\mathrm{Alk} = \left[\frac{1000}{V_s}\right][(V_1\mathrm{N}) - (V_s + V_1)[\mathrm{H}^+]] \quad \text{where,} \tag{2}$$

V_s is the volume of the sample of sea water, V_1 the volume of HCl to which the water sample was added, N the normality of the acid, and $[\mathrm{H}^+]$ the hydrogen ion concentration after the addition of the sea water to the acid.

Example: If 25.00 ml. of acid having a normality of 0.0100 are added to 100 ml. of sea water, the resulting solution shows a pH of 3.65.

$$3.65 = \log 1 - \log [\mathrm{H}^+]$$

$$\log [\mathrm{H}^+] = \bar{4}.35$$

$$[\mathrm{H}^+] = 0.000224$$

Substituting in (2)

$$\mathrm{Alk} = \frac{1000}{100}[(25.00 \times 0.01) - (100 + 25)\, 0.000224$$

$$\mathrm{Alk} = 10\,(0.250 - 0.028)$$

$$\mathrm{Alk} = 2.22$$

THE ALKALINITY-CHLORINITY FACTOR

The alkalinity of a sample of sea water gives useful and desirable information. However for comparing the alkalinities of a series of

samples of sea water whose concentrations vary, it is more expedient to express the value as a ratio to the chlorosity[1] of the water by

$$\frac{\text{Alk}}{‰\ \text{Cl}\left(\frac{\sigma_{20}}{1000}+1\right)} = K \text{ where,}$$

Alk is the alkalinity per liter of sea water at 20° C., ‰ Cl is the chlorinity per kilogram of sample, and $\left(\frac{\sigma_{20}}{1000}+1\right)$ is density of the water at 20° C.

The factor, K, is relatively constant but a deviation from an average value for it may indicate that important chemical changes have taken place in the water mass.

ACCURACY AND ERRORS OF THE METHOD

The pH measurements made with the glass electrode are readily duplicated and should never vary by more than 0.02 pH units. For average sea water samples this maximum variation is equivalent to 0.01 alkalinity unit (milligram atom of hydrogen). However in general routine determinations, the accuracies are equivalent to 0.005 alkalinity unit on duplicate determinations.

The volume of the sample should be measured with care. If an error of one per cent is made in the volume of a 100-ml. sample, it will produce a variation in the results by the procedure given above of 0.02 pH units.

At the pH range of the samples, 3.50–4.00, temperature changes were found to have little effect upon the actual determination. On three different samples run at various temperatures between 14° and 22°, the pH readings, while different for the samples, were constant. However, it is advisable that the determinations be made at laboratory temperature, because if the sample is below room temperature, there is a tendency for the condensation of atmospheric moisture on the electrode and the electrode assembly which may result in faulty readings.

[1] The term "chlorosity" has been recommended by the Committee on Chemical Methods and Nomenclature of the International Association of Physical Oceanography. The chlorosity of a sample of sea water is defined as the chlorinity multiplied by the density of the water at a given temperature. By international agreement, the chlorinity designates the grams of halides in a kilogram of water and is determined by titration with a silver nitrate solution which has been standardized against the standard water of the Hydrographical Laboratories of Copenhagen.

The existence of a salt error need not be considered when a glass electrode is used in the presence of a concentration of sodium ions similar to that occurring in sea water at a pH of 3.50 to 4.00. Ball and Stock (1) have shown that there is practically no difference between measurements made in hydrochloric acid solutions to which sea salts have been added, when the hydrogen electrode was used and when the glass electrode was employed.

The glass surface of the electrode is highly adsorbtive; therefore errors may result in measurements made in solutions having very marked differences in pH. The error may be eliminated by thorough and careful rinsing between determinations. Thus if the glass electrode has been used for making determinations of the actual pH of a series of sea water samples, the glass electrode should be well washed and rinsed before making observations for the alkalinity determination. Then observations should always be checked with another portion of the sample.

The atmosphere aboard ship or near the sea shore has a high humidity and special precautions are necessary to keep the vacuum tube compartment of the potentiometer well desiccated. Frequent regeneration of the desiccant is advisable.

CONCLUSIONS

1. The alkalinity of sea water is easily determined by means of the glass electrode. The employment of the glass electrode instead of color standards, as previously recommended greatly increases the accuracy of the determination.

2. The glass electrode assembly available on the market has been modified to facilitate the filling and emptying of the sample cup.

3. The effect of temperature on the pH readings obtained in the procedure given is negligible and no appreciable salt error is obtained.

4. A special sampler has been devised to insure accurate measurement of the water sample when taken for analysis under field conditions.

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THE PROBLEM OF THE DENSITY OF SEA WATER

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INTRODUCTION

The Density of Aqueous Solutions

The density of a solution can be determined easily and is of interest not only for its own sake but also in the calculation of other physical quantities. Many investigators have therefore determined the density and concentration of aqueous solutions. Of the older works, those of Kohlrausch, Kohlrausch and Hallwachs, Baxter and Wallace, and Lamb and Lee are outstanding for their precision.

Many attempts have been made to interpret the observed variations in the volumes of solutions calculated from the densities. If it is assumed that the volume of the solvent is not changed in forming a solution then the increase in volume resulting from the addition of a solute represents the volume of that solute. The volume change referred to one mole is called the apparent molal volume and may be calculated using the relation:

$$\text{Apparent Molal Volume} = \Phi = \frac{V_{solution} - V_{solvent}}{C}$$

If the concentration (C) is expressed as moles per liter of solution then $V_{solution} = 1000$, $V_{solvent} = \dfrac{1000\,d_1 - CM}{d_0}$ where d_0 is the density of the pure solvent, d_1 is the density of the solution at the temperature in question and M is the molecular weight of the solute. Therefore:

$$\Phi = \frac{M}{d_0} - \frac{1000\,(d_1 - d_0)}{C\,d_0} \qquad \text{Eq. 1}$$

For non-electrolytes such as sugar the apparent molal volumes vary slightly with concentration and are of approximately the same magnitude as the volume of a mole of pure solute.

The apparent molal volumes of electrolytes change rapidly with concentration and in dilute solution are usually much less than the molal volume of the pure solute. In not a few instances negative values of Φ are found (magnesium sulfate, sodium hydroxide). This

of course shows that the original assumption of constancy of volume of the solvent is incorrect. Attempts have been made to explain the changes in volume on solution in terms of the compression of the solvent by the charged ions (electrostriction). Baxter (*1.*) in reviewing the work up to 1911 sums up as follows: "The existing data show beyond question that the phenomena which take place are complex. Since these phenomena include both contraction and expansion at least two important influences must be at work . . . at any rate the following two changes take place during solution and dissociation: (a) The salt is freed in large part from compression due to chemical affinity and to molecular cohesion. (b) When the ions and probably the molecules are combined with water both the hydrated substance and the water undergo compression. The latter effect varies regularly with the compressibilities of the substances involved as well as their affinities for each other. . . ."

At least one very interesting property of the apparent molal volumes at infinite dilution ($\Phi°$, obtained by extrapolation to zero concentration of the curve of Φ vs. some function of the concentration) was discovered very early: the volumes are additive for the ions. While it is not possible to determine experimentally the volume of any ion,[1] the apparent molal volume at infinite dilution of any salt can be calculated from the values of three other properly chosen salts. For example, $\Phi°_{K_2SO_4} = 2\Phi°_{KCl} + \Phi°_{Na_2SO_4} - 2\Phi°_{NaCl}$. If an arbitrary value is assigned to the volume of any one ion the volumes of all other ions are determined.

The usefulness of the above concept was limited by lack of knowledge of the relationship between Φ and C. It was not until 1929 that Masson (*11.*) discovered empirically that over very large concentration ranges the apparent molal volume is a linear function of the square root of the concentration:

$$\Phi = \Phi° + mC^{1/2}.$$

It is very surprising that this relationship was not discovered much earlier. Kohlrausch and Hallwachs (*8.*) were looking for a relationship for apparent molal volumes and chose the cube root of the concentration as the variable, although Kohlrausch discovered the square root law for equivalent conductivity.

The Masson relationship was independently discovered by Geffcken (*3.*) and has been thoroughly checked by Scott (*15.*) and others.

[1] The equivalent conductivity of an electrolyte at infinite dilution is also an additive property of the conductivities of the ions. In this case knowledge of the transference numbers makes possible the assignment of definite values to the equivalent conductivity of each ion. No such method is available for Φ.

Further advance was made when Redlich and Rosenfeld (*13.*) derived from the Debye-Hückel theory the relationship between the *partial* molal volume and the square root of the volume concentration. The Redlich-Rosenfeld equation not only gave the same concentration variable ($C^{1/2}$) but also predicted the magnitude of the slope, the way in which valence type of the solute would affect the slope and the effect of change of solvent. The derived equation was:

$$\overline{V}_2 = V_2^0 + q\omega^{3/2}C_v^{1/2}$$

where q is a complex factor determined by the temperature and the properties of the solvent, and ω is one-half the summation of the number of ions times the square of the valence of the ion. The equation may be rewritten:

$$\overline{V}_2 = V_2^0 + q\omega\mu_v^{1/2} \qquad \text{Eq. 2}$$

where $\omega C_v = \mu_v$, the volume ionic strength of the solution. While applying strictly only to extremely dilute solutions the relationship has been of great value in interpreting results at moderate concentrations.

The partial molal volume referred to above is defined as the rate of change of the volume of the solution with respect to moles of a constituent ($\overline{V}_n = \partial V/\partial n_n$). It is also the increase in volume of an infinite volume of solution due to the addition of one mole of the constituent being considered. At infinite dilution ($C_v = 0$) the apparent and partial molal volumes become identical. At other concentrations the partial molal volumes can be calculated from the apparent molal volumes or the density data using methods developed by Gucker (*5.*) or Gibson (*4.*). For dilute solutions Geffcken (*3.*) has shown that $q\omega^{3/2} = 3/2$ m. (Eq. 3). The partial molal volume of the solvent can be calculated from the partial molal volumes of the solutes.

As an important deduction from the relationship discovered by Masson, Root (*14.*) proposed the following equation for expressing the densities of solutions in terms of concentration:

$$d_1 = d_0 + a'C + b'C^{3/2} \qquad \text{Eq. 4}$$

where a' and b' are constants. Over very wide concentration ranges it is sometimes necessary to include an additional term in C^2 but ordinarily density data can be very accurately expressed by the simple Root formula. For purposes of plotting to establish the constants the equation can be rearranged to give

$$\frac{1000\ (d_1 - d_0)}{C} = a + bC^{1/2}. \qquad \text{Eq. 5}$$

The densities of solutions containing more than one solute have been studied by but a few investigators. Two series of investigations however refer directly to the present discussion.

Bremner, Thompson and Utterback (*2.*) determined the densities of two mixtures (NaCl-KCl and NaCl-$MgSO_4$) in which the ratios of the two salts were kept constant and at the value found in sea water. Their results were expressed by means of the Root equation where the variable was the total equivalent concentration.

Wirth (*18.*) has shown that the *partial* molal volumes of potassium chloride, potassium bromide and potassium sulfate in sodium chloride solutions depend on the total volume ionic strength of the solution as predicted by the Redlich-Rosenfeld equation. The apparent molal volumes are greater in the mixed solutions than in pure solutions of the same total concentration. The increase is roughly proportional to the concentration of the sodium chloride in the mixture. These results show the value of the partial molal volume over the apparent molal volume which has no real physical significance. In solutions containing two or more solutes the apparent molal volume of a given solute becomes more and more difficult to define and measure, whereas the partial molal volume is a definite determinable quantity no matter how many components are present.

APPLICATION TO SEA WATER

The basic data of Knudsen and coworkers (*7.*) used in the preparation of the Hydrographic Tables were determined with extraordinary precision. The choice of samples, however, does not seem to be so fortunate as the density of dilute sea water is based entirely on samples from the Baltic Sea. Work by Thompson and Wirth (*17.*) showed that experimentally determined densities were higher by 0.02 σ_0 units than those calculated from the Knudsen equation. Use of 1930 atomic weights largely compensated for the difference. As samples of rather high chlorinity (18–22) were used, no check was made on the applicability of Knudsen's values to dilute sea water.

If the assumption of constant ion ratios in sea water is made then the total equivalent salt concentration present in any sample of sea water is given by the relation: $C_v = k\ Cl_v$.[2] Substituting in the Root equation, the density of sea water should be given by an equation of the type:

[2] It has been found that density relationships can be expressed more simply if volume concentrations are used. The chlorinity per liter (Cl_v) will therefore be employed throughout the present discussion.

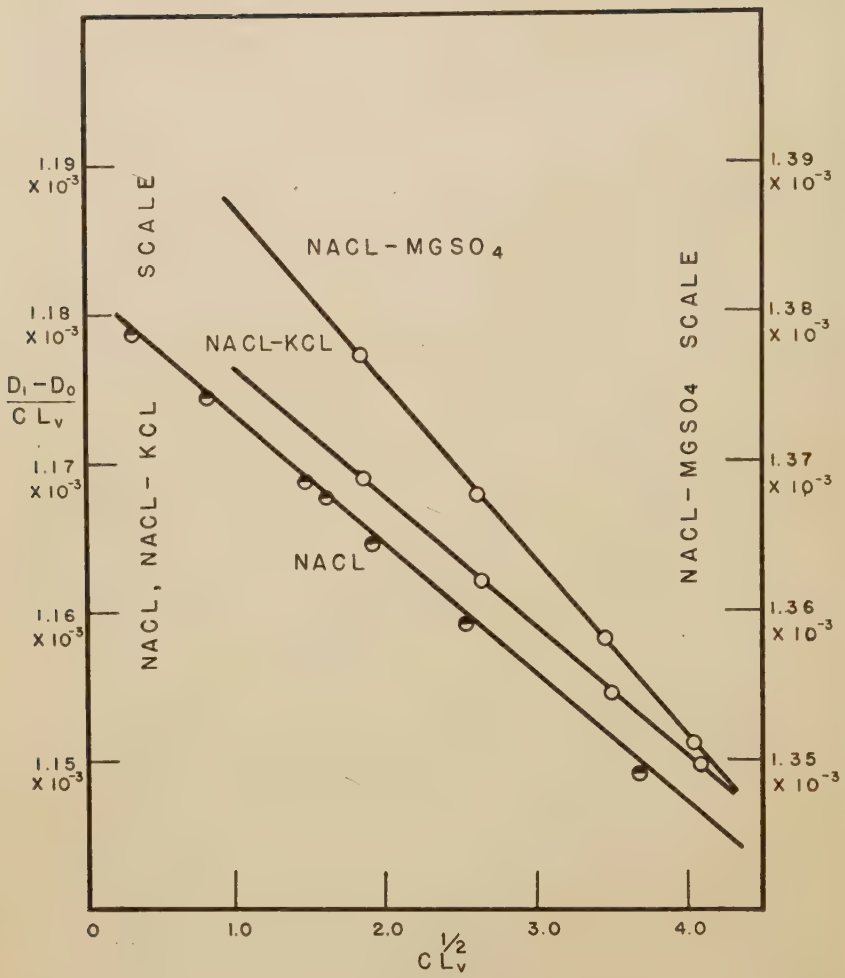

Figure 57. Results of Bremner, Thompson and Utterback for mixtures of NaCl and $MgSO_4$, and NaCl and KCl and for NaCl alone compared with the results of Kruis for NaCl. (25° C.)

$$\frac{1000\,(d_1 - d_0)}{\mathrm{Cl_v}} = A + B\,\mathrm{Cl_v}^{1/2} \qquad \text{Eq. 6}$$

Figure 57 shows that the data of Bremner, Thompson and Utterback (*2.*) for mixtures of NaCl-KCl and NaCl-$MgSO_4$ (where the mole ratios were kept constant and only the total concentration varied) can be represented by such an equation with $\mathrm{Cl_v}^{1/2}$ as the

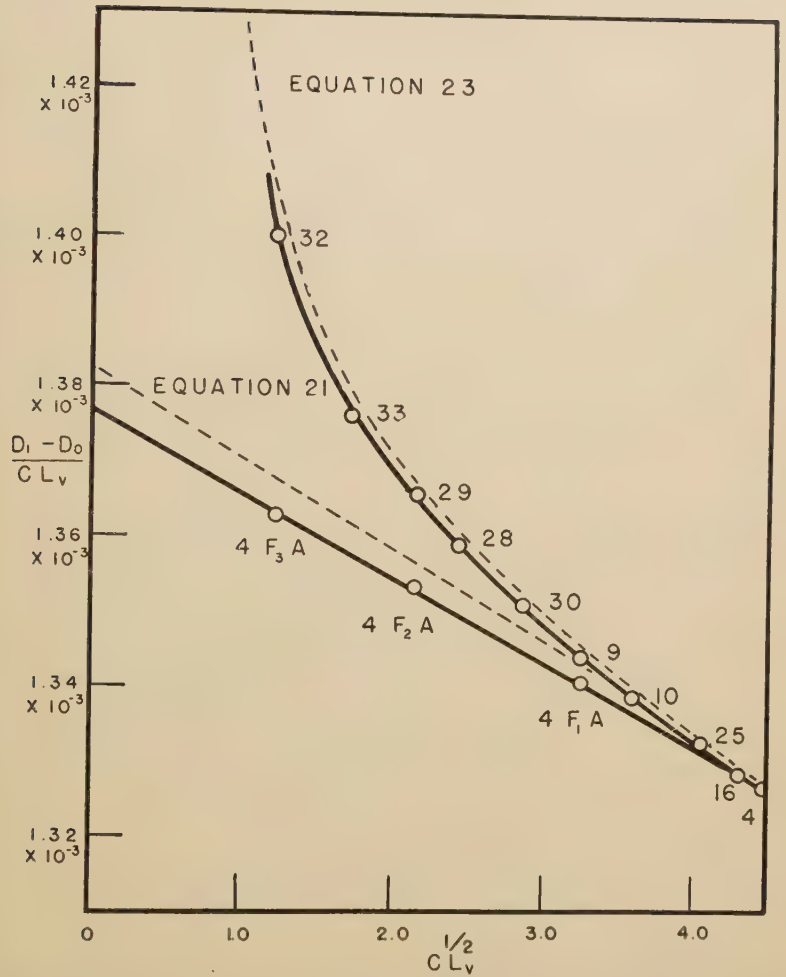

Figure 58. Experimental data of Knudsen for the density of sea water. (25° C.) Numbers are Knudsen's sample numbers. The 4F series was prepared by diluting Sample 4 with distilled water. The derived equations are represented by the dashed curves.

variable. On plotting the original data of Knudsen a curve is obtained which apparently will not intersect the Y-axis (Fig. 58).

Knudsen also determined the densities of a series of samples prepared by diluting a North Sea sample with distilled water. These values, also shown in Figure 58, deviate widely from the natural sea water from the Baltic Sea and can be represented by an equation of the correct theoretical form.

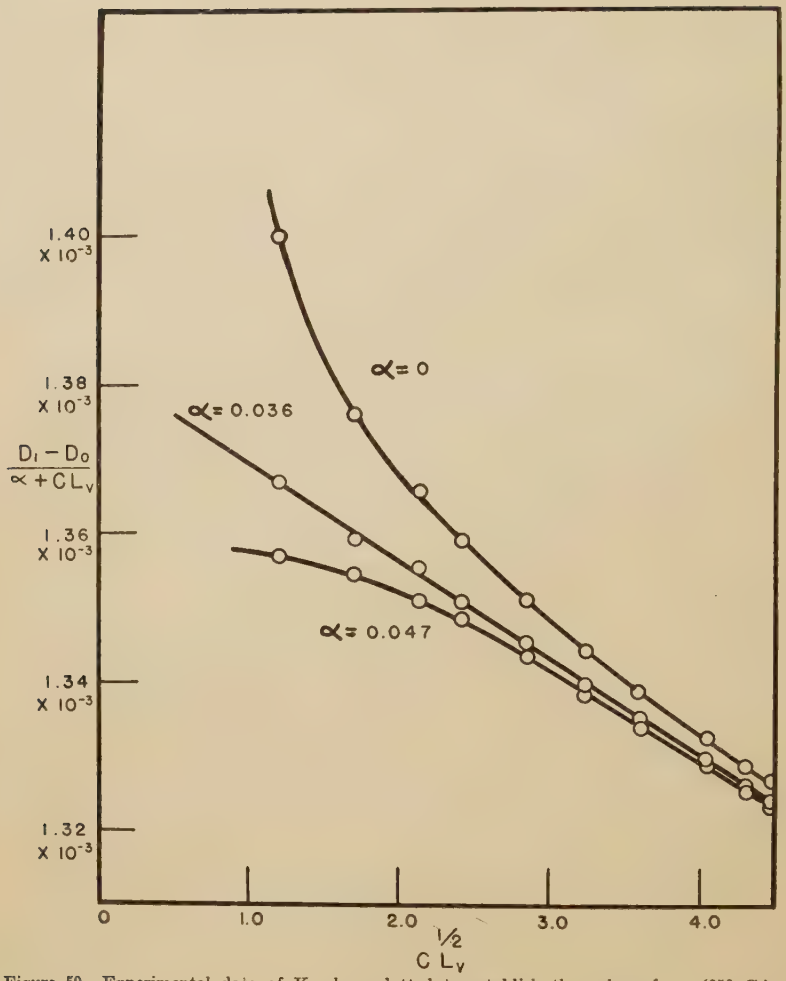

Figure 59. Experimental data of Knudsen plotted to establish the value of α. (25° C.)

The wide spread between the curve for sea water diluted with distilled water and the natural sea water can be attributed to natural dilution with water containing relatively more dissolved salts in proportion to its chloride content than is found in sea water. This is of course the actual condition where sea water is diluted with river water which normally contains $CO_3^=$, Ca^{++} and Mg^{++} and relatively little Cl^-. The effect of this dilution has been thoroughly discussed by Lyman and Fleming (*10.*) for the water of the Baltic and

they have developed equations giving the concentrations of the $SO_4^=$, Ca^{++}, Mg^{++} and HCO_3^- ions in terms of the chlorinity. These equations have the same form as the salinity equation of Knudsen and Sorensen (7.):

$$S = 0.030 + 1.8050\ \mathrm{Cl}$$

If a concentration variable of this type is substituted in the Root equation, the following is obtained:

$$\frac{1000\ (d_1 - d_0)}{\alpha + \mathrm{Cl_v}} = A + B\ (\alpha + \mathrm{Cl_v})^{1/2}. \qquad \text{Eq. 7}$$

If α is small compared to $\mathrm{Cl_v}$ and B is also small compared with A, then

$$\frac{1000\ (d_1 - d_0)}{\alpha + \mathrm{Cl_v}} = A + B\ \mathrm{Cl_v}^{1/2}. \qquad \text{Eq. 8}$$

α can be determined by plotting various values of $(d_1 - d_0)/(\alpha + \mathrm{Cl_v})$ against $\mathrm{Cl_v}^{1/2}$ and choosing the value of α which most nearly gives a straight line. Figure 59 shows a series of such plots. At 25° C. the equation that will best fit the data of Knudsen is

$$\frac{1000\ (d_1 - d_0)}{0.0360 + \mathrm{Cl_v}} = 1.38271 - 0.013121\ \mathrm{Cl_v}^{1/2}. \qquad \text{Eq. 9}$$

This represents the experimental data with an average deviation of five parts per million in the density.

At 0° C. the best equation is:

$$\frac{1000\ (d_1 - d_0)}{0.0307 + \mathrm{Cl_v}} = 1.49828 - 0.018289\ \mathrm{Cl_v}^{1/2}. \qquad \text{Eq. 10}$$

This equation represents the experimental data with an average deviation of 3.7 parts per million in the density, whereas Knudsen's equation:

$$\sigma_0 = -0.069 + 1.4708\ \mathrm{Cl} - 0.001570\ \mathrm{Cl}^2 + 0.0000398\ \mathrm{Cl}^3 \qquad \text{Eq. 11}$$

represents the experimental data with an average deviation of 4.5 parts per million. Equation 10 has one less constant to be determined than Equation 11 and the constants can be obtained very accurately from large scale plots, whereas the method of least squares must be used in obtaining the constants in the Knudsen equation.

The value of α obtained is very dependent on the most dilute sample. Slight errors in the density determination also have pro-

portionately greater effect on $(d_1 - d_0)/(\alpha + \mathrm{Cl}_v)$ at these low concentrations. It is not surprising that the values of α are different at different temperatures.

The difference between the density of a diluted sea water found on the assumption (a) that the diluting water is distilled water and (b) that the diluting water is of the same kind as that diluting the Baltic amounts to about fifty parts per million when the chlorinity is less than ten. This is at least ten times the experimental error in the determination of density. Knudsen's equations should not be expected to give highly precise values where the character of the diluting water is unknown. It is to be emphasized that no criticism of the Knudsen relationships at relatively high chlorinities or for samples taken in the open sea is intended here. It is only where the sea water is greatly diluted that the applicability of constants found for the Finnish Gulf to any and all other diluting water is questioned.

DERIVATION OF THEORETICAL DENSITY EQUATION

Another approach to the problem is to attempt a calculation of the density of sea water from known densities of the constituents assuming (a) that the constituents are in constant ratio to the chlorinity or (b) that the concentrations of the constituents are given by the equations of Lyman and Fleming (*10.*).

The total volume of a sample of sea water is given by the relation

$$V = n_0\overline{V}_0 + n_1\overline{V}_1 + n_2\overline{V}_2 + n_3\overline{V}_3 + \ldots\ldots \qquad \text{Eq. 12}$$

where n_0 is the number of moles of water, n_1, n_2, . . . are the number of moles of each salt present and $\overline{V}_0$, $\overline{V}_1$, $\overline{V}_2$, . . . are the corresponding values of the partial molal volumes. For the purposes of this discussion it is more convenient to consider n_1, n_2, . . . as the number of equivalents of each ion present while $\overline{V}_1$, $\overline{V}_2$, . . . would be the corresponding partial "equivalent" volumes of the ions. If we consider sea water to be a solution of a single salt, then the concentration of this salt is $n(= \frac{1}{2}(n_1 + n_2 + n_3 + \ldots) = \frac{1}{2}\Sigma n_n)$ and has a partial equivalent volume $\overline{V}$, so that

$$\mathrm{V} = n_0\overline{V}_0 + n\overline{V}. \qquad \text{Eq. 13}$$

From equations 12 and 13:

$$\overline{V} = \frac{1}{\frac{1}{2}\Sigma n_n}(n_1\overline{V}_1 + n_2\overline{V}_2 + n_3\overline{V}_3 + \ldots). \qquad \text{Eq. 14}$$

By analogy to Equation 2 each partial equivalent volume can be represented by an equation of the type:

$$\overline{V}_n = \overline{V}_n{}^0 + q_n\omega_n{}'\mu_v{}^{1/2} \qquad \text{Eq. 15}$$

where $\overline{V}_n{}^0$ is the partial (or apparent) equivalent volume of the ion at infinite dilution, $\omega_n{}'$ is one-half the square of the valence of the ion divided by the valence,[3] and μ_v is the volume ionic strength of the solution.

Equation 15 can be expected to hold with accuracy for the alkali salts in sea water and probably also for the alkaline earth salts. It is known to be incorrect for solutions of hydrochloric acid in sodium chloride, and it is to be expected that deviations will be found whenever the slope of the partial molal volume-square root of concentration curve for the single solute differs largely from that predicted by the Redlich-Rosenfeld equation. Wirth (*19.*).

Introducing equations 15 into Equation 14

$$\overline{V} = \frac{n_1}{\frac{1}{2}\Sigma n_n}(\overline{V}_1{}^0 + q_1\omega_1{}'\mu_v{}^{1/2}) + \frac{n_2}{\frac{1}{2}\Sigma n_n}(\overline{V}_2{}^0 + q_2\omega_2{}'\mu_v{}^{1/2}) + \ldots \qquad \text{Eq. 16}$$

which can be rearranged to give

$$\overline{V} = \frac{1}{\frac{1}{2}\Sigma n_n}(n_1\overline{V}_1{}^0 + n_2\overline{V}_2{}^0 + \ldots) + \frac{\mu_v{}^{1/2}}{\frac{1}{2}\Sigma n_n}(n_1q_1\omega_1{}' + n_2q_2\omega_2{}' + \ldots) \qquad \text{Eq. 17}$$

The first term in Equation 17 is by analogy to Equation 14 equal to $\overline{V}^0$, the partial equivalent volume at infinite dilution of the theoretical salt present in sea water.

To evaluate the terms in Equation 17 either of two assumptions can be made. The first is that the ion ratios for the major ions present in sea water are constant. This should express the results found in the open ocean or for sea water diluted with distilled water. The second assumption is that the concentrations of the magnesium, calcium, sulfate and bicarbonate ions are given by equations of the form: Ion concentration $= E + F\ \mathrm{Cl}_v$. If the equations of Lyman and Fleming (*10.*) are used it should be possible to estimate the density of water from the Baltic Sea.[4]

[3] This takes into account the use of equivalent concentration as the variable.

[4] These equations are:

$$\mathrm{SO_4}\ ‰ = 0.0061 + 0.1391\ \mathrm{Cl}‰$$
$$\mathrm{Ca}\ ‰ = 0.0154 + 0.02025\ \mathrm{Cl}‰$$
$$\mathrm{Mg}\ ‰ = 0.0020 + 0.06684\ \mathrm{Cl}‰$$
$$\mathrm{HCO_3}\ ‰ = 0.0493 + 0.004755\ \mathrm{Cl}‰$$

Returning to the first asumption, in Table I are given the equivalent concentrations (n) of each of the major ions in sea water of chlorinity 19.00 as taken from Table III of Lyman and Fleming. The concentration at any other chlorinity is assumed to be n $Cl_v/19.00$. The total equivalent concentration ($\frac{1}{2}\Sigma n_n$) is 0.59360. The volume ionic strength ($\frac{1}{2}\Sigma\omega_n' n_n$) at $Cl_v = 19.00$ is 0.68360 and at any other chlorinity is given by $0.68360\ Cl_v/19.00$.

In Table II are given the apparent (and partial) equivalent volumes at infinite dilution ($\overline{V}_n^0$) of certain salts as calculated from density values appearing in the literature. On the assumption that the volume of the potassium ion equals the volume of the fluoride ion the individual partial equivalent volumes of the ions were calculated. The partial equivalent volume of the theoretical salt present in sea water ($\overline{V}^0 = \Sigma n_n \overline{V}_n^0 / \frac{1}{2}\Sigma n_n$) was found to be 13.854. This value is quite independent of the assumption as to the volume of the potassium ion.

The experimentally determined slopes ($\partial\Phi_n/\partial\mu_v^{1/2}$) for the single salts are also given in Table II. The slope for sodium chloride which has the greatest influence on the result was evaluated from the results of Kruis (*9.*) and of Wirth (*19.*) and represents the best value in the range 0.1–1.0 N, ignoring the change in slope at concentrations below 0.1 N. The value 16.56 for $\overline{V}_{NaCl}^0$ is consistent with this slope. The slopes characteristic of the ions were then calculated using the assumption that $\partial\Phi/\partial\mu_v^{1/2}$ for potassium ion equals $\partial\Phi/\partial\mu_v^{1/2}$ for fluoride ion. $\Sigma n_n(\partial\Phi/\partial\mu_v^{1/2})/\frac{1}{2}\Sigma n_n$ was found to be 2.063. Applying Equation 3, $\Sigma n_n q_n \omega_n'/\frac{1}{2}\Sigma n_n = 3/2(2.063)$.

Introducing these experimental values into Equation 17:

$$\overline{V} = 13.854 + 3/2\,(2.063)\,(0.68360/19.00)^{1/2}\,Cl_v^{1/2}$$

$$= 13.854 + 3/2\,(0.3913)\,Cl_v^{1/2} \qquad \text{Eq. 18}$$

The apparent equivalent volume of the theoretical salt in sea water will be given by:

$$\Phi = 13.854 + 0.3913\,Cl_v^{1/2} \qquad \text{Eq. 19}$$

Substituting in the defining equation for Φ (Equation 1) where M is given by $\Sigma n_n M_n/\frac{1}{2}\Sigma n_n = 58.044$ (Table I):

$$\frac{1000\,(d_1 - d_0)}{Cl_v} = \left[\frac{58.044}{0.99707} - 13.854 - 0.3913\,Cl_v^{1/2}\right]\frac{(0.99707)(0.5936)}{19.00}$$

$$= 1.3819 - 0.01219\,Cl_v^{1/2} \qquad \text{Eq. 20}$$

TABLE I

COMPOSITION OF SEA WATER

(Based on Tables and Equations of Lyman and Fleming)

Ion	n_n $Cl_v = 19$	n_n(*Equiv./Liter*) *As Function of* Cl_v	$\omega_n' n_n$ $Cl_v = 19$	$\omega_n' n_n$ *As Function of* Cl_v	$\frac{n_n M_n}{\frac{1}{2}\Sigma n_n}$	$n_n M_n$ *As Function of* Cl_v
Cl^-	0.53529	0.028174 Cl_v	0.53529	0.028174 Cl_v	31.974	0.9989 Cl_v
Br^-	0.00081	0.000042 Cl_v	0.00081	0.000042 Cl_v	0.109	0.0034 Cl_v
$SO_4^=$	0.05514	0.000127+0.002896 Cl_v	0.11028	0.000254+0.005792 Cl_v	4.462	0.0061+0.1391 Cl_v
HCO_3^-	0.00229	0.000808+0.000078 Cl_v	0.00229	0.000808+0.000078 Cl_v	0.236	0.0493+0.0048 Cl_v
F^-	0.00007	0.000004 Cl_v	0.00007	0.000004 Cl_v	0.002	0.0001 Cl_v
Ca^{++}	0.01996	0.000769+0.001010 Cl_v	0.03992	0.001538+0.002020 Cl_v	0.673	0.0154+0.0203 Cl_v
Mg^{++}	0.10460	0.000165+0.005496 Cl_v	0.20920	0.000330+0.010992 Cl_v	2.143	0.0020+0.0668 Cl_v
K^+	0.00972	0.000512 Cl_v	0.00972	0.000512 Cl_v	0.640	0.0200 Cl_v
Sr^{++}	0.00030	0.000016 Cl_v	0.00060	0.000032 Cl_v	0.022	0.0007 Cl_v
Na^+	0.45902	0.024160 Cl_v	0.45902	0.024160 Cl_v	17.783	0.5556 Cl_v
$\Sigma =$	1.18720	0.00187 +0.062386 Cl_v	1.36720	0.00293 +0.071804 Cl_v	58.044	0.073 +1.8096 Cl_v

TABLE II

EQUIVALENT VOLUMES OF SALTS IN SEA WATER (25°)

Salt	$\overline{V}_{salt}^0$	$\frac{\partial\Phi}{\partial\mu_v^{\frac{1}{2}}}$	*Ion*	$\overline{V}_{ion}^0$	$\frac{\partial\Phi}{\partial\mu_v^{\frac{1}{2}}}$	$\frac{n_n\overline{V}_n^0}{\frac{1}{2}\Sigma n_n}$	$n_n\overline{V}_n^0$ *As Function of* Cl_v	$\frac{n_n(\partial\Phi/\partial\mu_v^{\frac{1}{2}})}{\frac{1}{2}\Sigma n_n}$	$n_n(\partial\Phi/\partial\mu_v^{\frac{1}{2}})$ *As Function of* Cl_v
KCl	26.74a	2.08	Cl^-	23.44_0	0.41	21.138	0.66039 Cl_v	0.370	0.01155 Cl_v
NaCl	16.56bc	1.945	Na^+	$-\ 6.88_0$	1.535	−5.320	−0.16622 Cl_v	1.187	0.03708 Cl_v
KBr	33.97a	1.85	Br^-	30.67	0.18	0.042	0.00131 Cl_v	0.000	0.00001 Cl_v
$\frac{1}{2}K_2SO_4$	16.14a	3.47	$\frac{1}{2}SO_4^=$	12.84	1.80	1.193	0.0016+0.03719 Cl_v	0.167	0.00023+0.00522 Cl_v
$NaHCO_3$	22. d	3.	HCO_3^-	28.9	1.5	0.112	0.0233+0.00225 Cl_v	0.006	0.00121+0.00012 Cl_v
KF	6.60e	3.35.	F^-	3.30	1.67	0.000	0.00001 Cl_v	0.000	0.00001 Cl_v
$\frac{1}{2}CaCl_2$	8.43f	1.99	$\frac{1}{2}Ca^{++}$	−15.01	1.58	−0.505	−0.0116−0.01517 Cl_v	0.053	0.00122+0.00160 Cl_v
$\frac{1}{2}MgCl_2$	7.25gh	1.84	$\frac{1}{2}Mg^{++}$	−16.19	1.43	−2.853	−0.0027−0.08900 Cl_v	0.252	0.00024+0.00786 Cl_v
			K^+	3.30	1.67	0.054	0.00169 Cl_v	0.027	0.00085 Cl_v
$\frac{1}{2}SrCl_2$	9.35g	1.73	$\frac{1}{2}Sr^{++}$	−14.09	1.32	−0.007	−0.00022 Cl_v	0.001	0.00002 Cl_v
					$\Sigma =$	13.854	0.0106+0.43223 Cl_v	2.063	0.0029 +0.06432 Cl_v

(a) Wirth (*18*), (b) Kruis (*9*), (c) Wirth (*19*), (d) International Critical Tables, (e) Geffcken (*3*), (f) Pesce (*12*), (g) Shedlovsky and Brown (*16*), (h) Herz (*6*).

In order to take into account the boric acid of which 0.004 moles are present in sea water of $Cl_v = 19.00$, it is assumed that its apparent molal volume does not depend on concentration and is equal to the molal volume of the solid (density of solid $= 1.44$). Then

$$\frac{1000\,(d_1 - d_0)}{C} = M - \Phi d_0 = 61.8 - \frac{61.8}{1.44} = 18.7$$

$$\frac{1000\,(d_1 - d_0)}{Cl_v} = \frac{(18.7)(0.0004)}{19.00} = 0.0004$$

Adding this to Equation 20,

$$\frac{1000\,(d_1 - d_0)}{Cl_v} = 1.3823 - 0.01219\ Cl_v^{1/2} \qquad \text{Eq. 21}$$

Equation 21 is plotted in Figure 58 and compared with the values found by Knudsen for North Sea water diluted with distilled water. The intercept for $Cl_v^{1/2} = 0$ is greater than the experimental value (1.3823 as compared with 1.3770). The calculated slope (0.01219) is greater than the experimental value (0.0112) by about 9%. Values of the density calculated using Equation 21 are compared with the experimental results of Knudsen in Table III. The maximum variation is 28 parts per million in the density.

The above calculation can be repeated on the assumption that the ion ratios for Ca^{++}, Mg^{++}, $SO_4^{=}$ and HCO_3^{-} are not constant. In Table I the concentration in equivalents per liter (Column 3), the volume ionic strength (Column 5) and the equivalent weight of the salt present in sea water (Column 7) are given as functions of the chlorinity. In Table II the equivalent volume at infinite dilution and the slope of the apparent equivalent volume-square root of volume ionic strength curve are also represented as functions of the chlorinity.

Introducing these functions into Equation 17:

$$\overline{V} = \frac{0.0106 + 0.43223\ Cl_v}{0.000935 + 0.031193\ Cl_v} + \frac{3/2(0.00147 + 0.035902\ Cl_v)^{1/2}\,(0.0029 + 0.06432\ Cl_v)}{0.000935 + 0.031193\ Cl_v} \qquad \text{Eq. 22}$$

Substituting the corresponding equation for Φ in Equation 1 and proceeding as before (Equations 19–20) the expression for the difference in density reduces to:

$$\frac{1000\ (d_1 - d_0)}{0.045 + \mathrm{Cl_v}} = 1.3786 - 0.01215\ (0.041 + \mathrm{Cl_v})^{1/2}$$

Correcting for the boric acid in the same manner as before, the final equation becomes:

$$\frac{1000\ (d_1 - d_0)}{0.045 + \mathrm{Cl_v}} = 1.3790 - 0.01215\ (0.041 + \mathrm{Cl_v})^{1/2} \quad \text{Eq. 23}$$

TABLE III

CALCULATED DENSITY OF SEA WATER

Knudsen's Sample No.	*Cl°/₀₀*	*Cl_v*	*$1000(d_1-d_0)$ Eq. 21*	*$1000(d_1-d_0)$ Eq. 23*	*$1000(d_1-d_0)$ Observed Knudsen*	*Difference*
			Sea Water Diluted With Distilled Water			
4	19.584	20.049	26.620		26.592	0.028
$4F_1a$	10.441	10.559	14.177		14.158	0.019
$4F_2a$	4.548	4.563	6.189		6.176	0.013
$4F_3a$	1.508	1.507	2.061		2.053	0.008
			Natural Sea Water			
23	22.237	22.846		30.237	30.212	0.025
21	20.415	20.923		27.450	27.731	0.019
4	19.584	20.049		26.615	26.592	0.023
16	18.142	18.537		24.649	24.626	0.023
25	16.020	16.323		21.766	21.752	0.014
10	12.842	13.030		17.455	17.443	0.012
9	10.410	10.528		14.163	14.150	0.013
30	8.089	8.155		11.022	11.017	0.005
28	5.837	5.867		7.978	7.973	0.005
29	4.608	4.624		6.316	6.314	0.002
33	2.927	2.931		4.041	4.033	0.008
32	1.474	1.473		2.070	2.062	0.008

In Table III the density differences calculated from this derived equation are compared with the experimental values of Knudsen (*7.*). Throughout the whole range of chlorinities the maximum difference found between the calculated and observed values is only 25 parts per million in the density. Equation 23 is also plotted in Figure 58.

It is very interesting that the calculated densities are uniformly *higher* than those found by Knudsen. This agrees almost exactly with the variation found experimentally by Thompson and Wirth (*17.*) at 0° C.

The excellent agreement obtained indicates that the Lyman and Fleming equations correctly represent the concentration relationships

in the Baltic Sea. It also shows the correctness of the method developed for obtaining the density of complex mixtures when the concentration can be expressed as a function of a single variable.

ACKNOWLEDGEMENT

The author wishes to express his deep gratitude to Professors Thomas G. Thompson and Clinton L. Utterback of the University of Washington Oceanographic Laboratories for the original suggestions which have led to this work and for their continued interest in it. The author also wishes to thank Dr. Richard H. Fleming of the Scripps Institution of Oceanography for supplying a copy of his paper in advance of publication.

SUMMARY

The original data of Knudsen on which the Hydrographic Tables are based have been examined on the basis of the modern theory of the density of aqueous solutions. The data can be made to fit a curve of the correct theoretical form only if it is assumed that the diluting water has a relatively greater salt content than indicated by the chlorinity.

The constant characteristic of the diluting water is believed to be applicable only to the dilute sea water from the Baltic Sea.

Equations have been derived using known physical constants of the constituents of sea water on the assumptions that (a) the ion ratios are constant and that (b) the ion concentrations are given by the equations of Lyman and Fleming. The first assumption leads to an equation which represents the density of sea water diluted with distilled water, while the second assumption leads to an equation representing the density of sea water found in the Baltic.

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CONVECTION AND SOARING OVER THE OPEN SEA[1]

By

ALFRED H. WOODCOCK

The transfer of momentum between the winds and the sea surface is a fundamental problem of oceanography. In the theoretical treatment of drift currents at sea and of the movements in the turbulent layer of air just above, no consideration seems to have been given to the possibility of a varying pattern of flow under unstable conditions. Recently Langmuir (1938) made measurements of "helical vortices set up by wind" in the surface waters of a lake. Lines of Sargassum weed, which are commonly seen on the central North Atlantic, were mentioned as an indication that similar vortices occur in the ocean. The observations of soaring flight presented below suggest that in unstable air at sea there are definite patterns which vary with the velocity and the stability of the wind.

There is some evidence that the force exerted by the wind on the sea surface cannot be expressed by a single continuous function of wind velocity and other factors, so that the critical values of these factors are also of interest to oceanographers. The soaring gulls seem to provide some clues as to the critical wind speeds at which there are marked changes in the form of convective motion, and thus in the transfer of momentum between the two mediums.

In a recent article on herring gull soaring (Woodcock, 1940), it was pointed out that the flight tactics of the birds vary with the wind and with the relative air and water temperatures. It was also suggested that the variations in flight routine of sea birds might be used to study some of the characteristic air motions over the water. In the present paper further data concerning gull soaring are presented.

The observations used here were made while on board the research vessel "Atlantis." They are confined to a sea area 30 to 600 miles off the east coast of the United States, between the latitudes 16° N. and 45° N. When cumulus clouds were forming, the layer of air in which the soaring was done extended upward from approximately 45 meters above the sea surface ("Atlantis" mainmast height) to the cloud base. Soaring altitudes greater than 620 meters have been measured with a range finder.

All of the air and water temperatures were measured with one

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thermometer; an ordinary laboratory thermometer graduated in whole degrees centigrade. Special care was exercised in making the air temperature measurements, in order to be sure that the thermometer was held to windward of the ship and adequately sheltered from the direct rays of the sun. The heights above the water of the air temperature measurements ranged from 3 to 7 meters. A dip bucket was used to obtain water for surface temperature measurements. Wind

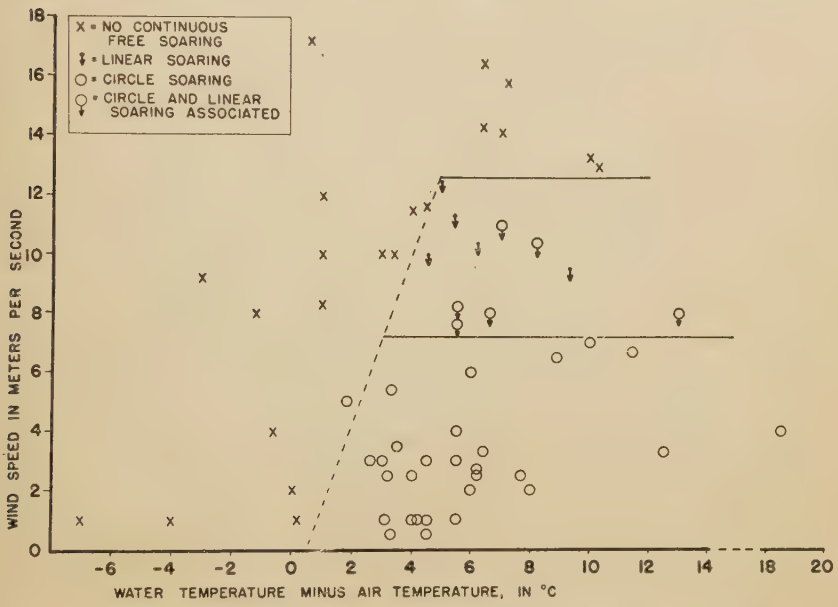

Figure 60. The flight response of herring gulls at different wind velocities and at various relative air and water temperatures.

velocity readings were made with a single anemometer at heights between 3 and 10 meters above the sea surface. Here again special precautions were taken to avoid areas where the ship's hull affected the air flow. (Correction for annemometer error has not been made, so the wind velocities are not absolute values.)

On Figure 60 the observations are plotted, with wind speed as ordinate and the temperature difference between the air and water as abscissa. Each observation represents a period of from 2 to 8 hours, with an average of about 6 hours. This does not mean that the birds were watched continuously for 6 hours, but that at any time during that period birds might have been seen performing the flight

routine which the symbol represents. The symbols on the graph differentiate three types of flight response.

One type is the absence of continuous, free soaring. *Continuous* soaring is here defined as soaring which extends over a sufficient length of time to show that the bird is not merely soaring by losing altitude. The term *free* indicates soaring which occurs independently of surface obstructions.

The second type of flight response is here called circle soaring. *Circle-soaring* is continuous, free soaring in which the birds circle about in horizontally restricted, chimney-like up-drafts, being carried along downwind (if there is a wind) at the same time.

The third type of flight may be called linear soaring. *Linear soaring* is continuous free soaring in which the birds move in a line directly against the wind flow. This soaring seems to be as nearly two-dimensional as it is possible for flight to be. Birds soaring linearly in the same up-draft are seen distributed in a vertical sheet parallel to the air flow. The thickness of the sheet seems to be not much wider than a few times the wing spread of the gulls.

The marks which are a combination of the circle and linear soaring symbols indicate that circle soaring was seen at the same time as linear soaring, though in a different location.

The scarcity of observations on the negative side of the temperature scale (Fig. 60) is not surprising when we consider the rarity of stability (U. S. Dept. of Agri. 1938, Chart No. 127) over the sea off our coast in the winter time. There was never any continuous free soaring when the air was warmer than the water. During these periods the birds spend most of their time sitting on the water, if the ship is stopped, or they alternate wing-flapping flight with resting on the water, if the ship is in motion. During periods when weak convection obtains, one often sees the birds test the up-drafts repeatedly, apparently trying to determine when the up-motion is again strong enough to make wing-flapping flight unnecessary. A few observations of frigate bird soaring among the West Indian Islands seem to show that these most efficient soaring birds use, in routine flight, convection up-drafts which apparently occur with much smaller temperature differences between the air and the water.

It will be noticed that 13 meters per second wind-speed marks the upper limit for herring gull soaring, and also that there is no linear soaring below 7 meters per second. There seems to be some very marked change in the form which the convective motion usually assumes at these two points.

Experimental work by Phillips and Walker (1932) with unstable

fluids has demonstrated that convection patterns are formed. These patterns vary; polygons being formed in horizontally motionless (without shear) fluids, with longitudinal and finally "strip-like cells" appearing as shear was introduced by horizontal flow. In unstable oil a further increase in shear caused the whole convection pattern to break down. In liquids it was found that the up-motion in the cells occurred in the centers, and the down-motion at the edges. In unstable air this was reversed, the up-motion being at the edges of the cells. In the strip-like cells formed in air, the up-moving current at the cell boundaries occurred in a sheet-like band extending up and down the direction of flow.

The change in the soaring tactics of the gulls at about 7 meters per second wind-speed, the sheet-like character of the up-drafts occurring between 7 and 13 meters per second wind-speed, and the total break-down of soaring conditions at about 13 meters per second wind speed, suggests that there is a similarity between the convection movements in the lower air and the experimental findings in unstable fluids.

Walker (1931, p. 413), in another paper in which he discusses Mal's work on forms of stratified clouds, says, "Mal's work has, I consider, transformed the interpretation of broken-up cloud layers as due to vertical instability from a plausible suggestion to an established fact; he has produced rectangular patterns and has shown that the types of cloud produced under different rates of shear resemble those formed in the laboratory." Perhaps convection patterns are also produced in the lower air, as the gulls seem to indicate.

Anticipating objections that these birds may be using some other known or unknown means of soaring, it should be brought out that there are three generally accepted (Horton-Smith, 1938, p. 98) requisites for soaring flight. If a bird is soaring, one of three things is happening: first, the air in which he soars may be rising; second, the bird may be descending; and third, the bird may be utilizing differences of horizontal velocity in the air. Here we want to show that we are dealing with the first condition.

In all of the observations here used the soaring gulls ascended many hundreds of meters into the air and stayed up for long periods of time. This quickly eliminates the second condition.

Concerning the third condition, i.e., horizontal differences of velocity in the air, Lord Rayleigh (1901, pp. 464 and 465) has said that while using "dynamical soaring" in strata of different relative velocities a bird must, upon entering one stratum, turn around until his direction is so reversed as to be with the wind of that stratum and contrary to the wind of the other stratum. But, in my observations

of circle soaring the birds turn both clockwise and counterclockwise in the same area at the same time. Soaring on differences in horizontal velocity depends upon the increase of wind with height (Idrac, 1925), and it is doubtful if this flight is possible far above the surface of the sea (Rayleigh, 1901, p. 465). But circle soaring depends upon temperature differences, and occurs hundreds of meters above the sea. Thus we see that there are several reasons why circle soaring cannot be dynamical soaring.

In linear soaring the birds do not circle, but move in an apparently straight line, and to high altitudes. This completes the elimination of numbers two and three of the required conditions for soaring flight, and leaves us with the first, i.e., up-moving air.

On January 5, 1939, at the approximate location of latitude 40° north and longitude 71° west, the "Atlantis" was in a favorable position for a measurement of an interesting down-wind tilt of an up-draft at a time when thirty or forty gulls had entered it successively. The birds were so well distributed that a rough measurement of an angle of tilt could be made with the ship's wire-angle indicator. An angle of 30° from the vertical was found. At this time the wind velocity was 6 meters per second, the water temperature 10° C., and the air temperature 3.9° C. The tops of the rising air columns appeared to be at cloud level, for occasionally birds were seen to pass through or behind wisps of cloud. During these rare occasions when many birds enter an up-draft consecutively, a sufficient portion of its extent is demarked to show that the air column has continuity, and is not just a rising bubble of unstable air. In light winds these rising columns of air closely approach the vertical. As the wind increases, they become tilted in the direction in which the air is moving.

Collecting data by noting flight variations has been a long slow process, involving hours of watching the birds go through their flight cycles and awaiting the chance coincidences of weather and nearby gulls to fill in gaps on the graph. However, if an observer could control the movements of his ship so as to remain in a region of violent meteorological change, he should be able to collect further data concerning the convection flow very quickly. Murphy (1936, see pp. 38–108) has shown the correlation between the distribution of sea birds and the great current systems of the sea and air. Soaring sea birds are also useful indicators of detailed small-scale air movements.

The occurrence of instability in the surface air over the oceans is wide-spread. In view of the possible importance of convection cells in affecting air and water movements, oceanographers should find it

useful to make a more thorough study of the convection patterns delineated by the gulls and other sea birds.

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THE MOTION OF ATMOSPHERIC DISTURBANCES ON THE SPHERICAL EARTH

By

B. HAURWITZ[1]

When the perturbations of the pressure distribution due to rapidly moving cyclones are eliminated by plotting charts of the mean distribution of the pressure for a number of days, centres of larger dimensions and of a more permanent character appear, as has been shown by the work carried out by Rossby and his collaborators (*7*). On winter maps of the northern hemisphere, as a rule at least five of these perturbations are found: the Icelandic and the Aleutian Lows, the Azores, Asiatic and Pacific Highs. They can hardly be considered as mere perturbations of the general circulation, but must rather be regarded as important parts of it, as is evidenced by their semi-permanent character. Nevertheless, they will in the following sometimes be referred to as perturbations or disturbances, since they are treated mathematically as perturbations of an undisturbed current.

Rossby (l. c.) has given a simple theory relating their dimensions and velocities with the zonal component of the general atmospheric circulation. He assumes that the lateral extent of these centres, that is their width in meridional direction, is infinite, and furthermore that the earth may be regarded as flat. The effect of the first simplification has been considered previously (*5*). The difference between the velocity of the centre and the undisturbed zonal velocity of the general circulation is smaller the smaller the lateral extent of the centre. Similarly, a centre of finite lateral extent becomes stationary at a smaller undisturbed zonal velocity than a centre of infinite lateral extent.

These centres extend over a considerable fraction of the earth's circumference. It appears necessary, therefore, to take the spherical shape of the earth into account. When the earth is regarded as a sphere it is also possible to allow for the change of the variation of the Coriolis parameter $2\omega \sin \varphi$ with the latitude. Hitherto the latitudinal variation of this parameter has been regarded as constant.

It would be possible to base a rigorous calculation on a previous investigation in which the wave motions on the rotating earth were studied (*4*). Instead, a much more simplified treatment will be

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given here. The formulae obtained are, of course, not strictly accurate. But the error is very small, especially when the number of waves around the earth's circumference is greater than four.

The atmosphere will be considered as incompressible for the sake of simplicity, although the results hold for any autobarotropic fluid or gas. Let ϑ be the colatitude, increasing towards S, λ the longitude, increasing towards E, a the earth's radius. The velocity of the zonal circulation of the atmosphere may be denoted by V. If α is the angular velocity of the air motion relative to the earth

$$V = \alpha a \sin\vartheta. \tag{1}$$

α will be assumed as constant for the sake of simplicity. u and v are the components of the perturbation velocity towards S and E. They may be small compared to V. The vorticity relative to the earth ζ is given by

$$\zeta = \frac{1}{a \sin\vartheta}\left\{\frac{\partial}{\partial\vartheta}[\sin\vartheta\,(v+V)] - \frac{\partial u}{\partial\lambda}\right\}. \tag{2}$$

The absolute vorticity, that is, the vorticity relative to the earth plus the vorticity due to the earth's rotation $2\omega\cos\vartheta$, must be constant

$$\zeta + 2\omega\cos\vartheta = \text{const.} \tag{3}$$

Differentiating with respect to time, it follows that

$$\left(\frac{\partial}{\partial t} + \alpha\frac{\partial}{\partial\lambda}\right)\left\{\frac{1}{a\sin\vartheta}\left[\frac{\partial}{\partial\vartheta}(\sin\vartheta v) - \frac{\partial u}{\partial\lambda}\right]\right\} + u\frac{\partial}{a\partial\vartheta}\left[\frac{1}{a\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta V\right)\right] = \frac{2\omega\sin\vartheta}{a}u. \tag{4}$$

The equation of continuity may be written in the form

$$\frac{1}{a\sin\vartheta}\left[\frac{\partial(\sin\vartheta u)}{\partial\vartheta} + \frac{\partial v}{\partial\lambda}\right] = 0 \tag{5}$$

This equation is not strictly correct since the existence of an undisturbed zonal velocity V implies the presence of a pressure gradient, and therefore a variation of the depth of the fluid, in meridional direction. But a more rigorous analysis based on the paper mentioned previously showed that this effect may be neglected without serious error.

The form of (5) suggests the introduction of a stream function χ by the equations

$$u = -\frac{\partial \chi}{a \sin \vartheta \, \partial \lambda}, \qquad v = \frac{\partial \chi}{a \partial \vartheta}. \tag{6}$$

Then (4) becomes

$$\left(\frac{\partial}{\partial t} + \alpha \frac{\partial}{\partial \lambda}\right) \frac{1}{\sin \vartheta} \left\{ \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial \chi}{\partial \vartheta} \right) + \frac{1}{\sin \vartheta} \frac{\partial^2 \chi}{\partial \lambda^2} \right\} + 2(\omega + \alpha) \frac{\partial \chi}{\partial \lambda} = 0. \tag{7}$$

Since perturbations progressing in easterly or westerly direction are to be studied, it may be assumed that

$$\chi(t, \lambda, \vartheta) = \cos(\beta t + m\lambda) f(\vartheta). \tag{8}$$

β is the frequency, m the wave number. The period

$$\tau = \frac{2\pi}{\beta}, \tag{9}$$

and the wave length

$$L = \frac{2\pi a \sin \vartheta}{m}. \tag{10}$$

If β is positive, the waves travel westward; if it is negative, they travel eastwards. Substituting the expression (8) for χ in the differential equation (7), it is found that $f(\vartheta)$ must satisfy the equation

$$\frac{1}{\sin \vartheta} \frac{d}{d\vartheta} \left(\sin \vartheta \frac{df}{d\vartheta} \right) + \left(\frac{2\omega m}{\beta + \alpha m} - \frac{m^2}{\sin^2 \vartheta} \right) f = 0. \tag{11}$$

At the poles f must vanish, since the value of χ must here be the same for every value of λ. This is only possible if f is an associated Legendre polynomial,

$$f = C \sin^m \vartheta \frac{d^m P_n(\cos \vartheta)}{d(\cos \vartheta)^m} = C \, P_n^m (\cos \vartheta), \tag{8a}$$

C being an arbitrary constant. Equation (11) is the differential equation of the associated Legendre polynomials if

$$\frac{2(\omega + \alpha) m}{\beta + \alpha m} = n(n+1); \qquad n = 1, 2, 3, \ldots \tag{12}$$

Thus, the length of the period $\frac{2\pi}{\beta}$ is given by (12). $d^m P_n(\cos \vartheta) / d(\cos \vartheta)^m$ is a polynomial in $\cos \vartheta$ of the degree $n - m$. It vanishes on $n - m$ parallels between the poles. If $n - m$ is odd, the equator is one of these nodal parallels; if it is even, P_n^m is different from zero at the equator. In either case, the nodal parallels are symmetrical to the equator.

When $n = m$ the nodal parallels vanish and the sphere is divided into sectors by the nodal meridians. The functions P_n^m are therefore called sectorial harmonics. It will be noted that always $m \leqq n$. If $0 < m < n$, the sphere is divided into quadrangles as shown in Figure 61. The functions P_n^m when $0 < m < n$ are the tesseral spherical harmonics. If $m = 0$, the nodal meridians disappear, and the functions P_n^0 are the ordinary Legendre polynomials or zonal spherical harmonics P_n.

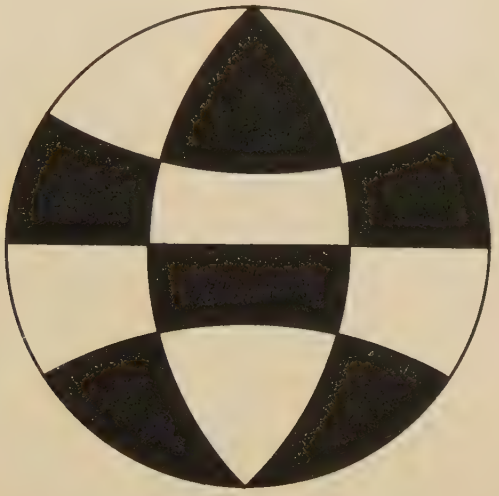

Figure 61. Tesseral spherical Harmonic; schematic.

Tables of the associated Legendre polynomials up to $n = 8$, $m = 8$, have been published by Tallquist (*9*) and by A. Schmidt (*8*). The numerical values of the functions published by both authors differ by a certain factor. Schmidt's form is preferable for numerical work because it is chosen so that the order of magnitude of the functions for different values of n and m remains the same. The position of the nodal parallels as taken from these tables is given in Table I. The tesseral functions P_n^n which have no nodal parallels are omitted.

The stream function for the perturbation motion is given by

$$\chi = C \cos(\beta t + m\lambda) P_n^m(\cos\vartheta) \tag{13}$$

and the stream function for the total, disturbed and undisturbed velocity

$$\chi + X = C \cos(\beta t + m\lambda) P_n^m(\cos\vartheta) - \alpha a \cos\vartheta. \tag{13a}$$

TABLE I

LATITUDE OF THE NODAL PARALLELS OF P_n^m

(The Functions P_n^n which have no Nodal Parallels are Omitted).

$n = 2$	$m = 1$	0°
$n = 3$	$m = 1$	±26.5°
	$m = 2$	0°
$n = 4$	$m = 1$	0°; ±40°
	$m = 2$	±22.2°
	$m = 3$	0°
$n = 5$	$m = 1$	±16.25°; ±50°
	$m = 2$	0°; ±35.3°
	$m = 3$	±19.5°
	$m = 4$	0°
$n = 6$	$m = 1$	0°; ±28°; ±56°
	$m = 2$	±14.5°; ±44°
	$m = 3$	0°; ±31.5°
	$m = 4$	±17.5°
	$m = 5$	0°
$n = 7$	$m = 1$	±12°; ±36.3°; ±60.5°
	$m = 2$	0°; ±35°; ±60°
	$m = 3$	±13°; ±39.8°
	$m = 4$	0°; ±38.7°
	$m = 5$	±16°
	$m = 6$	0°
$n = 8$	$m = 1$	0°; ±21.3°; ±42.5°; ±64°
	$m = 2$	±10.9°; ±32.7°; ±55°
	$m = 3$	0°; ±22.7°; ±46°
	$m = 4$	±12°; ±36.7°
	$m = 5$	0°; ±26.5°
	$m = 6$	±15°
	$m = 7$	0°

Figure 62. Perturbation stream lines for $n = 5$, $m = 2$. The centre of the figure is the pole, the outer circle the equator. Regions of different directions of motion are distinguished by full and broken curves.

The perturbation streamlines for $n = 5$, $m = 2$, are shown in Figure 62 as an example. The nodal meridians are 90° apart, the nodal parallels are at the equator and at 35.3° latitude. Thus the hemisphere is divided into eight cells. In each two adjoining cells the direction of the perturbation motion is opposite. The streamlines are drawn in arbitrary units. The distance between two streamlines is inversely proportional to the velocity of the motion.

In order to obtain the total stream function given by (13a), the term due to the undisturbed motion should be added to the function represented by Figure 62. If this is done, the streamlines surround the pole, and the effects of the perturbation appear as north-southerly undulations of the stream lines. The amplitude of this undulation depends on the constant C, which has to be regarded as arbitrary at present. (See also p. 264.)

When the stream function is known, the components of the perturbation velocity can be determined with the aid of the equations (6). The perturbation pressure is given by the equations of motion

$$(14)^2 \qquad \begin{aligned} \frac{\partial v}{\partial t} + \alpha \frac{\partial v}{\partial \lambda} + 2(\alpha + \omega) \cos \vartheta u &= -\frac{1}{\rho} \frac{\partial p}{a \sin \vartheta \, \partial \lambda} \\ \frac{\partial u}{\partial t} + \alpha \frac{\partial u}{\partial \lambda} - 2(\alpha + \omega) \cos \vartheta v &= -\frac{1}{\rho} \frac{\partial p}{a \partial \vartheta} \end{aligned}$$

With some simple transformations

$$(15) \quad p = C\, 2(\alpha + \omega) \cos(\beta t + m\lambda) \left[\frac{n+1}{n} \cos \vartheta \, P_n^m - \frac{n - m + 1}{n(n+1)} P_{n+1}^m \right].$$

From the geostrophic wind relation it follows that the undisturbed pressure

$$(16) \qquad P = P_0 + \rho a^2 \alpha \omega \sin^2 \vartheta.$$

This value of P has to be added to p to obtain the total pressure.

From the equations (9) and (10) for the period τ and the wave length L it follows that the velocity of the perturbation

$$(17) \qquad c = \frac{L}{\tau} = \frac{a \sin \vartheta}{m} \beta.$$

[2] These equations could have been used to derive (4) instead of the theorem that the vorticity must remain constant.

With the value of β given by (12)

$$c = \omega a \sin\vartheta \left[\frac{2}{n(n+1)} - \frac{\alpha}{\omega} \frac{n(n+1) - 2}{n(n+1)} \right] \tag{18}$$

The bracket represents the ratio of the velocity c of the disturbance to the velocity of a point fixed on the earth due to the earth's rotation. Table II gives values of the velocity for different n and α/ω

TABLE II

VELOCITY OF THE CELLS IN M/SEC AT 45° LATITUDE

n	2	3	4	5	6	7	8	9	10	11	12
α/ω = 1/10	87.4	27.4	+3.3	−8.7	−15.6	−19.6	−22.8	−24.8	−26.2	−27.3	−28.2
α/ω = 1/20	98.5	41.0	18.1	6.6	−0.03	− 4.0	− 6.8	− 8.7	−10.8	−11.2	−12.0
α/ω = 1/30	102.0	45.5	23.0	12.0	5.2	1.2	− 1.5	− 3.4	− 4.8	− 5.8	− 6.6

at 45° latitude. In considering this table, it should be kept in mind that for smaller wave numbers m and smaller n the approximation is not as good as for larger ones. However, this restriction does not seriously affect the present considerations. Positive figures indicate motion towards west, negative figures towards E, as can be seen from the form of the expression for χ (eq. (13)). If the zonal undisturbed current is zero, the motion of the disturbances is always westwards. This shows that these disturbances are identical with the oscillations studied by Margules (*6*) which are referred to as oscillations of the second class. The length of the period of these oscillations in sidereal days is given with sufficient approximation by

$$\tau = \frac{\beta}{\omega} = \frac{2m}{n(n+1)} \tag{4}$$

for the higher modes of oscillations. The same formula follows from eq. (12) if $\alpha = 0$. This type of oscillation is only possible on a rotating surface since the period becomes infinite when $\omega = 0$.

For smaller n, that is for disturbances of large dimensions, the motion is directed towards W, for smaller disturbances towards E. In the first case the effect of the latitudinal variation of the Coriolis force is preponderant, in the second case the effect of the undisturbed zonal velocity. For each disturbance n there is a certain velocity a_s of the zonal current at which the velocity of propagation vanishes. Then the disturbance remains stationary. It follows from (18) that

$$\frac{\alpha_s}{\omega} = \frac{2}{n(n+1) - 2}. \tag{19}$$

The values of α_s/ω and of the metric velocities at different latitudes are shown in Table III for some values of n. The last line contains the wave length of the disturbance—that is the extent of a high and the following low when $n - m = 0$; in other words, when the perturbations have their greatest possible lateral extent, from pole to pole.

The stationary velocity is smaller, the smaller the dimensions of the disturbance. The same rule holds for stationary disturbances of infinite extent on the flat earth according to the following formula given by Rossby (1939, eq. 22).

$$V_s = \frac{2\omega a}{m^2} \cos^3 \varphi.$$

The letters here have the same meaning as in the preceding formulae. The geographic latitude $\varphi = 90° - \vartheta$. This formula may be compared with (19) for the case of a spherical earth. To obtain the closest possible agreement of the assumptions involved in the derivation of both formulae, let the disturbance on the spherical earth extend from pole to pole so that $m = n$. From (19)

$$m = -\tfrac{1}{2} + \sqrt{\frac{2\omega}{\alpha_s}} \sqrt{1 + \frac{9}{8}\frac{\alpha_s}{\omega}}$$

since the negative root must be omitted. The ratio α_s/ω is small according to Table III. Therefore approximately,

$$m = \sqrt{\frac{2\omega}{\alpha_s}}$$

or if the expression (1) for the metric wind velocity is substituted

$$V_s = \frac{2\omega a \cos \varphi}{m^2}. \tag{20}$$

This expression agrees with the one derived by Rossby for a flat earth at the equator (and at the pole since here $V_s = 0$). It is to be expected that the formula for a flat earth gives the best approximation near the equator where the convergence of the meridians and the effect of the spherical shape of the earth are smallest. Moreover, the latitudinal variation of the Coriolis force—which has to be regarded as constant when the earth is assumed flat—changes least near

TABLE III

STATIONARY WIND VELOCITIES

n	2	3	4	5	6	7	8	9	10	11	12
a_s/ω	0.50	0.20	0.111	0.0715	0.050	0.037	0.0286	0.0227	0.0185	0.0154	0.0130
V_s at 30°	200.5	80.0	43.2	28.7	20.0	14.8	11.5	9.1	7.4	6.17	5.20 m/sec
V_s at 45°	164	65.5	36.4	23.5	16.4	12.1	9.4	7.45	6.06	5.05	4.26 m/sec
V_s at 60°	116.0	46.4	30.6	20.3	14.1	10.5	7.4	6.4	5.2	4.4	3.7 m/sec
L at 45° if $n = m$	14200	9450	7090	5660	4710	4050	3540	3140	2840	2580	2360 km

the equator. The approximation involved in the derivation of eq. (20) is better the smaller a_s/ω. a_s/ω decreases as n increases. Thus the effect of the spherical form of the earth decreases with decreasing dimensions of the perturbations, as is to be expected. In comparing the two formulae it should be remembered that Rossby's formula is based on the assumption that the zonal metric velocity is constant, while in this paper the angular velocity is considered as constant.

The mean pressure maps for February show two stationary highs and two lows in temperate latitudes on the northern hemisphere; the number m of disturbances around the earth's circumference is equal to two. According to Bjerknes (*2*) the angular velocity of the zonal current is nearly constant in temperate latitudes, and its maximum value in the troposphere is approximately 0.5×10^{-5} sec^{-1}, so that $a/\omega = 0.07$. It will be seen from Table III that this figure is very close to the approximate value for the stationary case, 0.0715 when $n = 5$. The perturbation streamlines would then be those shown in Figure 62, over which the streamlines of the undisturbed zonal motion have to be superimposed in order to obtain the total motion. The streamlines shown in Figure 62 are, of course, much more symmetrical than those which are observed in the atmosphere. Nevertheless, the close agreement of the actual angular velocity of the air with the theoretical stationary one for $n = 5$, $m = 2$, seems significant.

If the earth had a homogeneous surface, any of the disturbances given by (13) or a linear combination of these disturbances could exist. The heterogeneities of the earth's surface, in particular the unequal distribution of water and land, tend to set up perturbations whose location is determined by these geographical factors. The forces which generate the centres considered here are active especially

along the coast lines where the atmospheric solenoids are concentrated, as was discussed in a previous paper (*5.*).

If the effect of these solenoidal forces on the motion of the disturbances is to be taken into account, the left-hand side of (7) is not equal to zero, but to the external forces. Their intensity is mainly a function of the geographical distribution; only to a much lesser extent does it depend on the time. It can therefore be assumed that the force is represented by a function $F(\lambda, \varphi)$ of λ and φ only. Equation (7) becomes then an inhomogeneous equation whose solution is composed of two parts. The first is the solution of the homogeneous equation which is a linear combination of the expressions of the form (8). It represents the possible free oscillations of the fluid system. They are subjected to the damping influence of friction which eventually must bring the motion to a standstill. The second part consists of a particular solution of the inhomogeneous equation which can be found by well-known methods. It gives the perturbations generated by the external forces. They correspond to the forced oscillations of vibrating systems and will be referred to as forced disturbances. Since the generating force is independent of the time the forced disturbances are also independent of the time. It has been shown previously[3] that the stationary forced perturbations have the same wave lengths as the free stationary perturbations. The amplitude of a forced perturbation increases as the difference between the wave length of the free perturbation and of the generating force decreases. When the difference vanishes, the amplitude reaches a maximum; resonance occurs. This is analogous to the phenomenon of resonance in the case of harmonic oscillations, except that there the resonance is between the periods of the generating force and of the free oscillation. In the present case where the generating force is a function not of time, but of space, its wave length takes over the rôle of the period.

In the light of these considerations, the close agreement between the observed zonal velocity on the northern hemisphere during February and the theoretical stationary zonal velocity for the perturbations of the form $\cos 2\lambda\, P_5^2(\cos \vartheta)$ may be interpreted in the following manner. The distribution of the force over the earth can be represented by a series of spherical surface harmonics. The part of the solution which represents the effect of the generating force then appears as a series of terms each giving the effect of one of the members in the series development for the external force. The amplitudes of the terms depend on the amplitudes of the terms in the series for the

[3] B. Haurwitz: l. c.

generating force and on the degree of resonance. It may therefore be concluded that the agreement between the observed and the theoretical zonal velocity in the case mentioned previously is such a resonance phenomenon. Neither the generating force nor the resulting perturbation is exactly of the form $\cos 2\lambda\, P_5^2(\cos \vartheta)$. It is not even necessary that this term in the series development of the external force should have a very high amplitude. Nevertheless, due to resonance, the corresponding term in the series for the resulting perturbations reaches a very high amplitude. The other harmonic components of the force affect the solutions too, although not as much. But owing to their existence the stream function does not very closely resemble the symmetrical picture shown in Figure 62.

For a complete study it would be necessary to analyze the external force, similar to the methods of the tidal theory, and to see which components have wave lengths close to those of the free perturbations. These will be predominant and their amplitudes largest. Such an analysis may be rather difficult since the mathematical formulation of the effect of the generating solenoidal force is not quite obvious.

In the meantime it may be useful to determine the dominant terms by a more empirical method of trial and error, as has been done here in a particular case. A few more general ideas can, however, be formulated as a result of the theoretical considerations.

Equation (19) and Table III show that n is larger and thus the dimensions of the perturbation patterns smaller the smaller the zonal velocity α_s. The zonal velocity α_s may be taken as an index for the general circulation. It depends on the intensity of the meridional pressure gradient. Thus, with a strong circulation index (α_s large) there will be a few large centres. When the circulation is weak the perturbation pattern appears broken up into numerous smaller cells. These ideas agree with those developed by Rossby[4] for the plane earth, and with the results obtained by Allen (*1*) from a study of the five-day-mean-pressure charts. Allen's charts show a few strongly developed centres of high and low pressure when the zonal circulation is strong; in other words, when the meridional pressure gradient is intense. On the other hand, when the zonal circulation is weak, a great number of smaller pressure centres exist; the various "centres of action," like the Aleutian low and the Pacific high, appear broken up into two or more weaker centres.

A knowledge of the distribution of these centres of action and their development is essential if the weather development is to be forecast for a longer period. Thus, the zonal circulation intensity which ap-

[4] C. G. Rossby: l. c.

pears to regulate this pressure distribution can serve as a valuable help in long range forecasting.

The next step towards a solution of this problem is to derive a method by which the changes in the zonal circulation intensity can be determined in advance. The zonal circulation intensity depends, through the geostrophic wind relation, on the meridional pressure gradient which has been called the circulation index by Rossby. No satisfactory theory has been given yet to account for the variations of this quantity. If the view is accepted that the meridional pressure gradient is a result of the temperature differences between lower and higher latitudes, it would seem that its variations depend on the intensity with which heat is transported from lower to higher latitudes. Defant (*3*) has discussed how such a transport of heat can be effected by the cyclones of temperate latitudes. Using his concept of a horizontal mixing of colder northerly and warmer southerly air whereby the cyclones act as turbulent eddies, it may be assumed that at first when a strong zonal circulation exists intense centres of high and low pressure are present. Due to the horizontal mixing between high and low latitudes the meridional differences of temperature are reduced, the zonal current becomes smaller and the perturbation patterns break up into smaller, more numerous centres according to the results of the present investigation. With the breaking-up the horizontal mixing becomes less effective, so that now the temperature differences between north and south increase again. In this manner the variations between strong and weak zonal circulations with their effect on the large scale weather situation appear as a quasi-periodic process. The zonal circulation can only attain certain lower and upper limits. When these limits are reached it will be intensified or reduced again. Obviously, not very much regularity of the fluctuation can be expected in view of the many factors coming into play. But it should be possible by the development of the theory and an analysis of the weather situations to determine these factors and their importance, to that it becomes feasible to forecast, at least, say, at the peak of the circulation intensity, when the next minimum is to be expected, and vice versa.

SUMMARY

To eliminate the fast moving disturbances of smaller extent such as the cyclones of temperate latitudes, charts of the mean pressure distribution for five or more days may be plotted. These charts show the semi-permanent centres of action, for instance, the Icelandic and Aleutian Low and the Pacific and Azores High. The slow changes of position and intensity of these centres determine the large scale

variations of the weather. The spherical shape of the earth and the variation of the deflecting force of the earth's rotation with the latitude determine the horizontal dimensions of the possible cells of high and low pressure and their velocity with respect to the general zonal motion of the atmosphere. For each possible distribution of cells there is a zonal velocity of the atmosphere at which the system remains stationary. If the position of the semi-permanent highs and lows is fixed and determined by the distribution of water and land, and if the zonal velocity of the atmosphere is of the right magnitude, their intensity will be strengthened, provided that the "forced" distribution of the cells coincides with the possible "free" distribution on a homogeneous earth. This is similar to the strengthening of forced oscillations which are in resonance with free oscillations.

When the zonal circulation is strong, the intensity of the semi-permanent centres of high and low pressure is great, and the number of centres is small. When the zonal circulation is weak, these centres break up into smaller and less intensive centres. A mechanism is suggested which may account for the observed changes between times of strong and weak zonal circulation.

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EFFECT OF DELAYED TITRATION ON THE SALINITY DETERMINATION

By

E. F. THOMPSON

Wüst (1932) has discussed the effect of storage on the chlorinity of samples. He compared the results from samples examined almost immediately at sea with those titrated in the shore laboratory after a considerable period of time. He concludes that there is a definite tendency for the chlorinity to increase on storing. The effect was largest with sample bottles that had been previously titrated and, therefore, no longer full; and least with full bottles on which the stoppers had been covered with paraffin wax. In the case of the incompletely full bottles the mean increase of chlorinity was 0.011‰ while in the case of the full bottles with paraffined stoppers it was only 0.002‰. For many purposes, as, for instance, the exploration of relatively unknown waters, such small differences can be of little importance but in the investigation of well known areas and, particularly, in cases where the seasonal and long period changes of the physical characters are sought, even such small effects may be of the same order of magnitude as those which are being examined.

It is frequently impossible and very often inconvenient to examine samples for salinity immediately. Further, a ship board laboratory seldom, if ever, reaches the same convenience for analysis as that found on shore. In connection with the present investigation of the fluctuations of the Gulf Stream and in consideration of the relatively homogeneous waters of the Sargasso Sea, small differences of salinity are obviously of considerable importance. It seemed desirable to determine whether the effect of storage is as great in this region as Wüst had found in his observations.

On 5th January 1939 at "Culver" station 106, samples were collected in the usual manner; but from 100, 496, and 905 meters, as many sample bottles as could be filled were obtained. The sample bottles had been carefully examined and washed with water from the same respective depths from a previous haul so that a small amount of rinsing with the actual sample was sufficient.

The titrations were performed in the manner set out by Oxner and Knudsen (1920) and the greatest care was taken to avoid errors. The apparatus was carefully cleaned to eliminate erratic drainage and the readings were made with a special burette magnified so that the interpolation of the last figure could have some degree of probability.

While many observers titrate to a definite color, the present worker has found from experience that such a procedure depends upon the observer's power to memorize the particular tint. This power is very variable in different workers and even in the same worker during different stages of the examination. The usual tendency is for the accepted end point color to become darker as fatigue sets in. Quite small changes in the light also effect the apparent tint. The procedure adopted here was to titrate until there was the first definite permanent *change in tint* as compared with standards. The possible effect of changing light was eliminated by using constant artificial illumination. The stock potassium chromate solution was freed from possible chloride contamination in the usual way by the addition of a drop of silver nitrate.

Before a sample bottle was opened, the stopper was rinsed with distilled water and wiped dry. The failure to observe this precaution is probably the cause of many anomalous salinity results.

A great deal has been said by various workers about the possibility of evaporation during examination. Wüst (1932) goes so far as to consider that this effect is so great as to eliminate the advantages of repeated titrations. The present author had found previously that samples which had come to temperature equilibrium with the laboratory showed no measurable change after being left open for four hours; and it would seem, then, that the erratic results often obtained in repeated titrations are more probably due to contamination through careless manipulation. When the sample undergoes vibration or shaking, as at sea, or is subject to large temperature changes, quite large salinity changes occur through a faulty stopper within quite a short space of time.

For the standardization of the silver nitrate, two tubes of normal sea water were used. The tubes were examined for small defects, such as small cracks in the tips, and then each tube was titrated three times. At the end of the titrations, three more titrations were carried out on each tube, thus giving six titrations for each normal water tube. In no case was there any appreciable difference between the means of the two sets of six titrations. This great care in standardization is necessary as any error in the standardization will appear in all the samples examined. One of the chief reasons why repeated examinations of a sample often add nothing to the accuracy is that there has been an error in standardization.

The first set of examinations on the samples was carried out a few hours after collection and each sample was titrated five times. It is well known to all analysts that, in repeated titration of the same

sample, there is an unconscious tendency to return the same figure. This is well seen in the ability of an analyst to obtain excellent agreement between duplicate titrations performed successively and failure when the duplicate examinations are separated by a time interval or by other examinations. In an attempt to minimize this effect the samples were examined successively so that the same sample appeared only every fourth time. Another advantage of this procedure is that any sustained trend, such as tiring of the observer, will be felt equally by each sample.

For the correction of the chlorinity and the conversion to salinity, Knudsen's (1901) data were used but, as the interpolation is too crude for the present investigation, smoothed curves were constructed for the required ranges. The samples were examined first in January; and subsequently in February, March, and April. On each occasion a new sample bottle was used and the process repeated in exactly the same manner. The results are given in Table I.[1]

TABLE I

Depth of sample (meters)	Salinity Determinations °/₀₀								
	Month of titration								*Grand Mean*
	January		*February*		*March*		*April*		
		Mean		*Mean*		*Mean*		*Mean*	
100	36.588		36.579		36.600		36.577		
	36.601		36.599		36.586		36.596		
	36.594		36.593		36.579		36.600		
	36.585		36.587		36.581		36.575		
	36.592		36.583		36.604		36.582		
		36.592		36.588		36.590		36.586	36.589
496	36.326		36.324		36.333		36.314		
	36.309		36.338		36.326		36.331		
	36.330		36.311		36.320		36.335		
	36.332		36.317		36.318		36.335		
	36.327		36.329		36.337		36.323		
		36.325		36.324		36.327		36.328	36.326
905	35.191		35.169		35.220		35.196		
	35.197		35.217		35.215		35.176		
	35.202		35.203		35.174		35.196		
	35.210		35.201		35.193		35.174		
	35.179		35.195		35.198		35.188		
		35.196		35.197		35.200		35.186	35.195

[1] The results are given as salinity ‰. Except in the mean values, the last figure is almost certainly without significance.

It can be seen immediately that there is no general trend of the samples on storing. In no case does the difference between the grand mean for the sample deviate by 0.01‰ salinity from any monthly value, and in only one case, for the April examination of the 905 meter sample, is this value approached. If this value is omitted the extreme range of the four monthly means for any one sample is less than 0.005‰ salinity. A statistical examination[2] of the data shows that the differences between means for months for the same sample are without significance.

A similar examination of the effect of storage was made with samples collected in April and stored until May. Here again, it was found that storage did not effect the salinity of the sample.

Storage, then, does not effect the salinity value of samples if due care is taken in their collection and storage. It should be pointed out that this conclusion has been established for the Bermuda region only. Whether it is true for other areas is still unknown. It is possible that in waters in high latitudes where the spring plankton is often very dense, and in places where stored samples are subjected to great climatic changes, this may not be so, and an examination of this possibility seems desirable.

These results should not be taken as justification for postponing titration without adequate reason; where there is any question of the satisfactory nature of the sample bottles, delay in titrating may produce enormous errors. But, provided this possibility does not arise, the effect of storage is negligible.

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